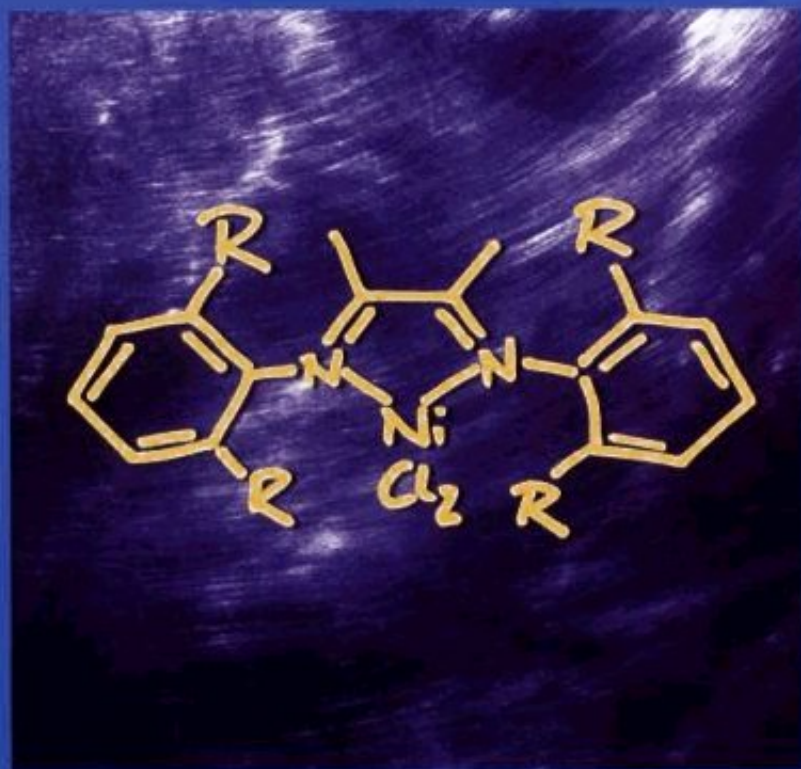


Late Transition Metal Polymerization Catalysis

Bernhard Rieger, Lisa Saunders Baugh, Smita Kacker,
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Contents

Preface XI

List of Contributors XII

1	Nickel Polymerization Catalysts with Ylide Steering Ligands	1
	<i>Aleksander Ostoja Starzewski</i>	
1.1	Introduction	1
1.1.1	Ylides and Ylidic Bond Systems	1
1.1.2	Ylide Ligand Properties and Coordination Modes	3
1.2	Ylide Nickel Complexes: Novel Polymerization Catalysts	5
1.2.1	Ylide Nickel Complex Synthesis	6
1.2.2	Spectroscopy	6
1.2.2.1	NiPh(Ph ₂ PCHCPhO)(Me ₃ PCH ₂) 1a	7
1.2.3	X-ray Structure Analysis	8
1.3	Ethylene Polymerization	10
1.3.1	Catalyst Activity	10
1.3.2	Novel Ligand Control of PE Molecular Weight	11
1.3.3	Linear and Branched Macromolecules	13
1.3.3.1	Linear Macromolecules	13
1.3.3.2	Short Chain-Branched Macromolecules	13
1.3.3.3	Long Chain-Branched Macromolecules	14
1.3.4	Styryl-Terminated Oligo-/Polyethylenes	15
1.4	Cycloolefin Polymerization	16
1.5	Butadiene Polymerization	17
1.6	Polar Monomer Polymerization	17
1.7	Acetylene Polymerization	18
1.7.1	Catalyst Activity	18
1.7.2	MATPAC, Novel Highly Polar Matrix Polyacetylenes	18
1.7.3	POLPAC [®] , a Tailor-made Polyacetylene Application	22
1.7.4	MATPAC for NLO Devices	23
1.8	References	24

2	Microstructure Control of Ethene Homopolymers Through Tailored Ni,Pd(II) Catalysts 27
	<i>Jürgen Kukral, Alexandra Abele, Gabi Müller, and Bernhard Rieger</i>
2.1	Introduction 27
2.2	Novel 2,6-Diaryl-Substituted Diimine Catalysts: A Versatile Concept for Tailored Polymer Properties from Simple C ₂ Monomers 31
2.2.1	Ligand and Complex Synthesis 32
2.2.2	Solid State Structures 33
2.2.3	Ethene Polymerization Experiments 37
2.2.3.1	Palladium Monomethyl Complexes 37
2.2.3.2	Nickel Dibromides 37
2.3	Desymmetrized Palladium and Nickel Diimine Catalysts 40
2.3.1	Ligand and Complex Synthesis 40
2.3.2	Polymerization Reactions 41
2.4	Palladium Complexes with Bidentate P∩N-Ligands: Application in Ethene Oligomerization 43
2.4.1	Synthesis and Characterization 44
2.4.2	Ethene Oligomerization Reactions 46
2.5	Application of Sterically Demanding Bis(phosphino) Complexes in Ethene Homopolymerization 47
2.5.1	Synthesis and Complexation of Ethene Bridged Bis(phosphine) Ligands 47
2.5.2	Solid State Structures 49
2.5.3	NMR Studies on the Palladium Dichloro Species 52
2.5.4	Influence of Substitution on Ethene Polymerization Reactions 52
2.6	Conclusion 55
2.7	References 56
3	Highly Active Ethene Polymerization Catalysts with Unusual Imine Ligands 59
	<i>Gerrit A. Luinstra, Joachim Queisser, Benno Bildstein, Hans-Helmut Görtz, Christoph Amort, Michael Malaun, Alexander Krajete, Gerald Werne, Marc O. Kristen, Norbert Huber, and Christoph Gernert</i>
3.1	Introduction 59
3.2	Ligand and Metal Complex Synthesis 62
3.2.1	Diimine Systems 62
3.2.1.1	[N,N] Diimines Containing Peripheral N-Heteroaromatic Substituents 62
3.2.1.2	1,2-Diimine Ligands with N-Hetaryl Substituents 64
3.2.1.3	Nickel Complexes with N-Hetaryl 1,2-Diimine Ligands 65
3.2.1.4	Diimine Nickel and Palladium Complexes with 2,6-Dibromophenyl Groups 67
3.2.2	Diimine Pyridine Systems 71

3.2.2.1	[N,N,N] Bis(imino)pyridine Iron and Cobalt Complexes with Peripheral N-Heteroaromatic Substituents	71
3.2.2.2	N-Halogenoaryl-Containing Tridentate Ligands and their Fe Complexes	75
3.2.3	Salicylimine Systems	75
3.2.3.1	[N,O] Salicylimine Nickel Complexes Containing Peripheral N-Heteroaromatic Substituents	75
3.2.4	Ethanol Imine Ligands and their Nickel Complexes	79
3.3	Polymerization Performance	82
3.3.1	Diimine Ni Complexes with Peripheral N-Heteroaromatic Substituents	83
3.3.2	Diiminepyridine Iron and Cobalt Complexes with Peripheral N-Heteroaromatic Substituents	84
3.3.3	Diimine Palladium and Imine Pyridine Iron Complexes with Halogenophenyl Imine Ligands	87
3.3.4	Salicylimine Ni Complexes	91
3.3.5	Hydroxyimine Ni Complexes	91
3.4	Concluding Remarks	95
3.5	Acknowledgements	95
3.6	References	95
4	Cycloaliphatic Polymers via Late Transition Metal Catalysis	101
	<i>Brian L. Goodall</i>	
4.1	Introduction	101
4.2	The Addition Polymerization of Cyclic Olefins	104
4.2.1	Cyclopropenes and Cyclobutenes	104
4.2.2	Cyclopentene	104
4.2.3	Norbornenes	105
4.2.3.1	Nature and Scope of the Catalyst	107
4.2.3.2	Reaction Injection Molding (RIM) of Norbornenes	108
4.2.3.3	Catalyst Synthesis and Polymerization of Norbornene	109
4.2.3.4	On the Mechanism of Initiation	110
4.2.3.5	Poly(norbornene) Microstructure	112
4.2.3.6	On the Mechanism of Propagation and Chain Transfer	113
4.2.3.7	Isolation and Characterization of Norbornene Oligomers	119
4.2.3.8	Control of Glass Transition Temperature	123
4.2.3.9	Multi-Component Catalyst Systems	125
4.2.3.10	Polymerization of Norbornenes Containing Functional Groups	137
4.2.3.11	Polymer Properties and Applications	139
4.3	The Copolymerization of Norbornenes with Acyclic Monomers	144
4.3.1	Copolymers with α -Olefins	144
4.3.1.1	Nickel Catalysts	145
4.3.1.2	Palladium Catalysts	147
4.4	References	150

5	Well-Defined Transition Metal Catalysts for Metathesis Polymerization	155
	<i>Michael R. Buchmeiser</i>	
5.1	Introduction	155
5.2	Transition Metal Alkylidenes	156
5.2.1	Group IVA and VA Transition Metal-Based Initiators	156
5.2.2	Group VI Transition Metal-Based Initiators	157
5.2.2.1	Chromium-Based Initiators	157
5.2.2.2	Tungsten-Based Initiators	157
5.2.2.3	Molybdenum-Based Initiators	161
5.2.3	Group VIIA Transition Metal-Based Initiators	170
5.2.3.1	Rhenium-Based Initiators	170
5.2.4	Group VIIIA Transition Metal-Based Initiators	170
5.2.4.1	Ruthenium-Based Initiators	170
5.2.4.2	Reactivity of Ruthenium-Based Initiators	171
5.2.4.3	Ligand and Structural Variation in Ruthenium-Based Initiators	174
5.2.5	Osmium-Based Initiators	183
5.3	Outlook	183
5.4	References	183
 6	 Catalysis in Acyclic Diene Metathesis (ADMET) Polymerization	 193
	<i>Stephen E. Lehman Jr. and Kenneth B. Wagener</i>	
6.1	Introduction	193
6.2	The ADMET Reaction	195
6.2.1	ADMET: A Step-Growth Polycondensation	195
6.2.2	Functional Group Tolerance	197
6.2.3	Formation of Cyclics	197
6.2.4	<i>Trans</i> -Metathesis	198
6.2.5	General ADMET Mechanism	199
6.2.6	Regiochemical and Stereochemical Considerations	201
6.2.7	Applications of ADMET	202
6.3	Classical Metathesis Catalysts	203
6.4	Well-Defined Tungsten and Molybdenum Catalysts	204
6.5	Well-Defined Ruthenium Catalysts	207
6.5.1	Early Observations: Ill-Defined Ruthenium-Based Catalysts	207
6.5.2	First-Generation Grubbs Catalysts: $\text{RuCl}_2(\text{PR}_3)_2\text{CHR}_1$	208
6.5.2.1	Synthesis and Activity	208
6.5.2.2	Use in ADMET	210
6.5.3	Second-Generation Grubbs Catalysts: $\text{RuCl}_2(\text{NHC})(\text{PR}_3)\text{CHR}_1$	211
6.5.3.1	Synthesis and Activity	211
6.6	Mechanism of ADMET with Grubbs Catalysts	214
6.6.1	Role of the Phosphine Ligand: $\text{RuCl}_2(\text{PR}_3)(\text{L})\text{CHR}_1$	214
6.6.2	Role of the L Ligand: $\text{RuCl}_2(\text{PR}_3)(\text{L})\text{CHR}_1$	217
6.6.3	Role of the Carbene: the Special Case of the Methylidene	219
6.6.4	Stereochemical Aspects of ADMET	221
6.6.5	Catalyst Decomposition	223

6.7	Experimental Considerations for ADMET	224
6.7.1	The Ideal Case: Bulk ADMET with High Vacuum	224
6.7.2	The Ideal Case: Bulk ADMET with Carrier Gas	224
6.7.3	ADMET with Volatile Monomers	225
6.7.4	Viscous or Solid Monomers of Polymers	225
6.8	Conclusions and Outlook	226
6.9	References	226
7	Transition Metal-Catalyzed Polymerization in Aqueous Systems	231
	<i>Stefan Mecking and Jérôme P. Claverie</i>	
7.1	Introduction	231
7.1.1	Traditional Free-Radical Polymerization in Aqueous Systems	231
7.1.2	General Aspects of Transition Metal-Catalyzed Polymerization in Aqueous Systems	235
7.2	Catalytic Olefin and Alkyne Polymerization in Aqueous Systems	237
7.2.1	Historical Development	237
7.2.2	Recent Progresses in Catalytic Insertion Polymerization of Olefins	238
7.2.2.1	Alternating Olefin/Carbon Monoxide Copolymerization	239
7.2.2.2	Polymerization of Ethylene and 1-Olefins	243
7.2.2.3	Miscellaneous Insertion Polymerizations	249
7.2.3	Recent Progresses in Ring Opening Metathesis Polymerization	231
7.2.4	Recent Progresses in Catalytic Polymerization of Alkynes	254
7.2.4.1	Introduction	254
7.2.4.2	Catalytic Polymerization of Alkynes in Aqueous Systems	256
7.2.5	Summary	258
7.3	Controlled Free-Radical Polymerization in Aqueous Systems with Metal Complexes	259
7.3.1	General Features of Atom Transfer Radical Polymerization (ATRP)	259
7.3.2	Polymerization of Water-Soluble Monomers by ATRP	261
7.3.3	Polymerization of Water-Insoluble Monomers of ATRP	264
7.4	Polymerization by Suzuki-Coupling in Aqueous Systems	266
7.5	Conclusions and Outlook	268
7.6	References	270
8	Copolymerization of Carbon Monoxide with Alkenes	279
	<i>Giambattista Consiglio</i>	
8.1	Introduction	279
8.2	Copolymerization Catalysts and Mechanism	280
8.3	Structure of the Olefin/Carbon Monoxide Copolymers	283
8.4	Catalyst Precursors for the Copolymerization of Ethene	283
8.5	Copolymerization of 1-Olefins	288
8.5.1	Copolymerization of Styrene (and Homologues)	288
8.5.2	Copolymerization of Propene (and Other Aliphatic Olefins)	294
8.6	Copolymerization of Internal and Cyclic Olefins	297
8.6.1	Cyclopolymerization of α,ω -Dienes	299

8.7	Conclusions	300
8.8	References	301

9 Strategies for Catalytic Polymerization of Polar Monomers 307
Ayusman Sen and Myeongsoon Kang

9.1	Introduction	307
9.2	Results and Discussion	307
9.3	Conclusion	316
9.4	References	316

Subject Index 319

Preface

Modern polymerization catalysis, as we know it, was triggered by the development of metallocenes and the concomitant understanding of relationships between ligand structure and polymer properties. The manipulation of these useful relationships has led to a renaissance in the synthesis of polyolefin materials having new stereoregularities and, therefore, precise control of polymer rheology.

In contrast to Group IV-based polymerization catalysts, late transition metal complexes can carry out a number of useful transformations above and beyond the polyinsertion reaction. These include isomerization reactions and the incorporation of polar monomers, which have allowed the synthesis of branched polymer chains from ethylene alone, and of functional polyolefins via direct copolymerization. The rational design of metallocene catalysts allowed, for the first time, a precise correlation between the structure of the single site catalyst and the microstructure of the olefin homo- or copolymer chain. A similar relationship does not yet exist for late transition metal complexes. This goal, however, and the enormous opportunities that may result from new monomer combinations, provide the direction and the vision for future developments.

The present book contains nine chapters focusing on the design of imine and phosphorylide catalyst structures, the preparation of cycloaliphatic materials, polar/nonpolar monomer copolymerizations, organometallic polymerizations in aqueous media, and current frontiers in ROMP and ADMET processes. Exactly forty years after the Nobel Prize for Ziegler and Natta, we give a concise description of the state of the art in these fascinating and rapidly developing fields. The authors present, likewise, viewpoints from the forefront of both academia and industrial research, so that basic science and polymer applications are equally covered.

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1

Nickel Polymerization Catalysts with Ylide Steering Ligands

ALEKSANDER OSTOJA STARZEWSKI

Abstract

Ylide ligands in nickel catalysts possess a remarkable steering power. Bis(ylide)-nickel complexes provide nonionic organometallic catalyst architectures, which efficiently suppress chain transfer and termination reactions and instead promote chain growth in ethylene polymerizations. Pronounced ligand effects are observed concerning catalyst activity, molecular weight and branching behavior. The catalyst activities without co-catalysts are remarkable in unpolar and even in highly polar solvents. The polar group tolerance makes these catalysts suitable for a variety of polar monomers. Polyacetylene can now be prepared in a controlled fashion in stabilizing highly polar matrices and, in this way, becomes easily processible and even water soluble – ready for high tech applications.

1.1**Introduction****1.1.1****Ylides and Ylidic Bond Systems**

Charge distributions and energy levels of phosphorus ylides can be described as the result of specific donor–acceptor interactions between phosphanes and carbenes, resulting in highly polar dative phosphorus–carbon bonds with varying degrees of π -contribution. Similar orbital interactions are also operative with other donor atoms such as nitrogen, arsenic, sulfur or iodine in complexes with carbenes (i.e. in nitrogen, arsine, sulfur ylides), with nitrenes (i.e. in phosphine-imines, arsine-imines, sulfimines), and with oxygen (i.e. in phosphine-oxides, sulfoxides). As a consequence all of these ylidic bond systems exhibit dramatically lower first ionization potentials than normal π -bonds: trimethylphosphine-methylene 6.8 eV versus ethylene 10.5 eV, trimethylphosphine-imine 8.3 eV versus azomethine 12.4 eV, trimethylphosphine oxide 9.9 eV versus formaldehyde 14.4 eV [1–7].

The extreme bond system of phosphorus–carbon ylides, indicated in Eq. (1), is reflected in outstandingly low first ionization potentials (Tab. 1.1).

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Photoelectron spectroscopic data place this class of isolable energy-rich compounds on the very top of an energy scale of ligands that do not have a net charge. The molecular property “IE₁” is a quantitative description for the energetic availability of an outermost valence electron and thus a prominent feature of reactivity.

Within a molecular orbital approximation, the electron is ejected from the highest occupied molecular orbital (HOMO). Molecular orbital calculations at various levels of sophistication describe the highest occupied MOs of most ylides as being strongly localized on the ylidic carbon. Exceptions to this are found for example in cyclopentadienide derivatives, where the orbital of corresponding symmetry is the HOMO-1 (IE₂). In terms of reactivity, the low first ionization potentials of ylides reflect high oxidizability, high proton affinity, and basicity. UV photoelectron spectra in conjunction with detailed molecular orbital calculations for each individual ylide structure have made possible a rationalization of the different substituent and heteroatom effects.

Tab. 1.1 Gas-phase UV-PES vertical ionization potentials IE₁ (eV) of phosphorus and arsenic ylides (n_C⁺) and related phosphines (n_P).^{a)}

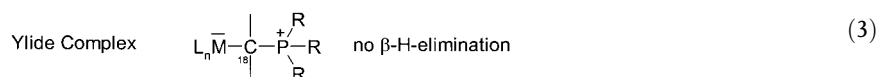
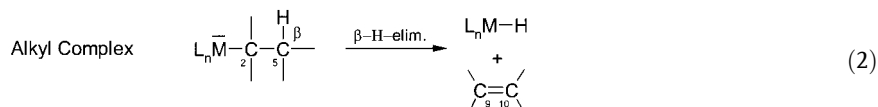
		<i>R</i> = <i>Me</i>	<i>R</i> = <i>Ph</i>
R ₃ PCHCHCHMe	n _C ⁺	6.02	5.95
R ₃ PCHCHCHPh	n _C ⁺	6.20	
R ₃ PCHCHCH ₂	n _C ⁺	6.20	
R ₃ PCHPh	n _C ⁺	6.19	6.01
R ₃ PCHMe	n _C ⁺		6.15
R ₃ PCH ₂	n _C ⁺	6.81	6.62
R ₃ PCHSiMe ₃	n _C ⁺	6.81	6.71
R ₃ PCH(SiMe ₃) ₂	n _C ⁺	6.92	
R ₃ AsCH ₂	n _C ⁺	6.72	
R ₃ AsCHSiMe ₃	n _C ⁺	6.56	
R ₃ AsC(SiMe ₃) ₂	n _C ⁺	6.66	
R ₃ PCp	π _{C=C} /n _C ⁺	6.82/7.02	6.66/6.91
R ₃ PC(CN) ₂	n _C ⁺		7.63
R ₃ P	n _P	8.60	7.80

a) Abbreviations: Me=methyl, Ph=phenyl, Cp=cyclopentadienyl; “n_C” designates ionization from an orbital with largest coefficient on the ylide carbon; “n_P” designates ionization from the phosphorus lone pair orbital.

1.1.2

Ylide Ligand Properties and Coordination Modes

The above-mentioned features of ylides, together with the ability to form ylide anions, and their ease of synthesis make them exciting and versatile ligands for transition metal chemistry [8]. Ylides have outstanding potential with respect to the formation of transition metal–carbon bonds, because a major reaction path for the decomposition of such moieties, i.e. β -H elimination, is blocked by the phosphonium group, a significant difference in comparison with simple alkyl complexes [Eqs. (2) and (3); Fig. 1.1].



Ylides mostly act as σ -carbon ligands with practically no back-bonding characteristics. A variety of ylide–metal structural arrangements have been synthetically accomplished. The organometallic ylide chemistry (Fig. 1.1) covers most of the d-block and some f-block as well as main group elements. It includes mono-, di- and trinuclear

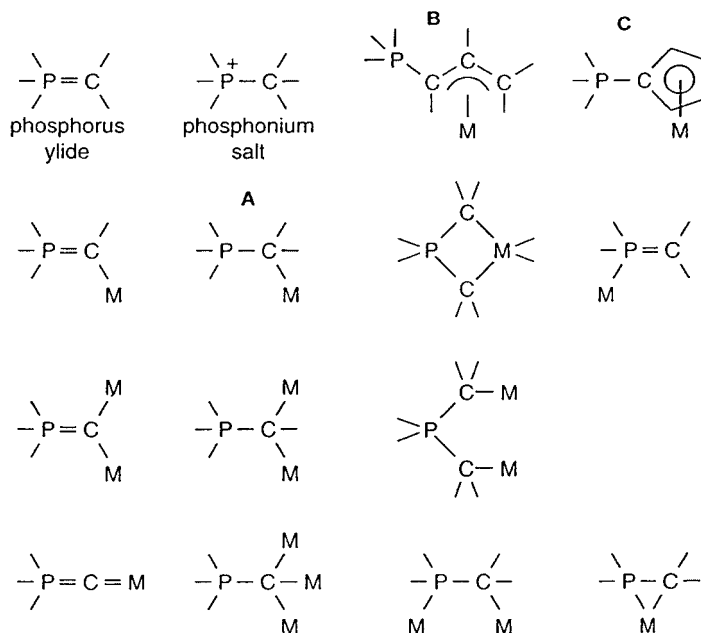


Fig. 1.1 Ylide coordination modes.

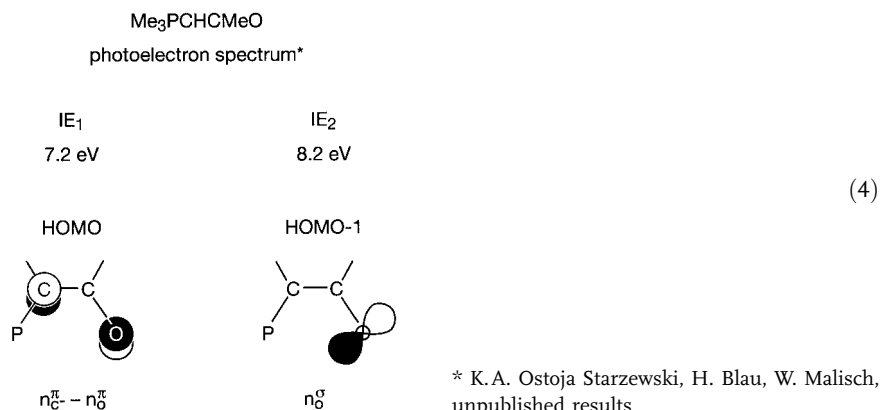
Tab. 1.2 (C=C) π vertical ionization potentials of conjugated ylides IE₂ or IE₁ and related π -hydrocarbons (IE₁).

	IE ₂ or IE ₁ (Ylide) ^{a)} [eV]	IE ₁ (π -Hydrocarbon) [eV]
Me ₃ P=CH-CH=CH ₂	9.02 (IE ₂)	Ethylene: 10.51
Me ₃ P=C ₅ H ₄	6.82 (IE ₁) !	Butadiene: 9.10
Me ₃ P=CH-C ₆ H ₅	8.32 (IE ₂)	Benzene: 9.25

a) Ionization from (C=C) π localized orbitals.

species with ylide ligands sometimes in bridging or in chelating function. In Fig. 1.1, **A** represents the fundamental monodentate σ -complex. Its metal-carbon bond can be described simply as the result of a two electron/two orbital stabilizing interaction between the high lying carbon-centered ylide HOMO “n_C” and a vacant metal orbital. For a given ylide, the degree of complex stabilization depends on the energy of the interacting metal orbital(s), which can be tuned chemically with the other ligands attached to the metal. In **B** and **C** hydrocarbon π -systems are attached to the ylidic carbon which not only results in a delocalization of electron density but also raises the energy levels of the π -substituents with respect to the unperturbed parent π -hydrocarbon, i.e., for the ligands in **B** and **C** relative to ethylene and *cis*-butadiene (Tab. 1.2). In the exceptional case of cyclopentadienylidenephosphoranes (R₃PC₅H₄) the extreme perturbation of the π -substituent pushes the corresponding *cis*-butadiene level even slightly above that of the ylide bond n_C-level.

The enhanced energetic availability of the substituent π -electrons makes it clear why strongly conjugated ylides may act as polyhapto π -ligands when metal localized orbitals of appropriate symmetry are accessible. In extreme cases the location of highest reactivity may shift into a position remote from the onium center. This “activation” of a substituent, attached to the ylidic carbon, is a general feature and is not limited to CC- π -systems. An impressive example is the photoelectron spectrum of acetylmethylene-trimethylphosphorane, where the low second ionization potential IE₂=8.2 eV originates essentially from an oxygen lone pair orbital [Eqs.



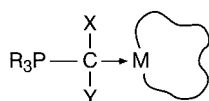
(4) and (5)]. The corresponding lone pair ionization IE_1 of acetaldehyde appears at 10.3 eV, that of formaldehyde at 10.9 eV.



1.2

Ylide Nickel Complexes: Novel Polymerization Catalysts

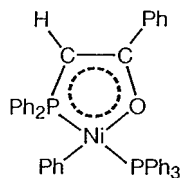
Obviously, ylide complexes such as **1**, in which the ylide ligand is coordinated via the ylidic anion center to a suitable transition metal, are of interest concerning their properties as polymerization catalysts in comparison to commonly used ligands such as phosphanes, which differ significantly in the energetic availability of the ligand lone pair electrons as well as in the ligand donor/acceptor ratio. This chapter reviews research results in this area, obtained in the Central Research Laboratories of Bayer in Leverkusen.



1 phosphorus ylide complex

The organometallic chemistry of nickel has been demonstrated to have outstanding potential in the activation of unsaturated substrates. Nickel-phosphane-based homogeneous catalysts for the CC-linkage of olefins are known to provide synthetic access to dimers, trimers, oligomers and cyclooligomers. Some of these catalysts offer a high degree of control over the stereochemistry of these transformations [9 a, b].

The reaction of the stabilized ylide benzoylmethylene-triphenylphosphorane with Ni(0) in the presence of triphenylphosphane leads to the *oligomerization* catalyst **2**, which catalyzes the reaction of 6000 moles of ethylene per mole of complex at 50 bar and 50 °C. The catalyst **2** is a model system for the “Shell Higher Olefin Process” (SHOP) for the production of liquid α -olefins of high linearity, which has been studied in detail by Keim and coworkers at the RWTH Aachen [9 c and literature, reviewed in 8].



2 phosphane nickel complex

This system was selected by us to serve as a benchmark for developing new ligand fields, based on the concept of highly polar ylidic bond systems, with the intention of turning low-valent nickel complexes into novel catalysts for *polymerization* instead of for oligomerisation, without the need for co-catalysts. It was hoped that such systems would provide a much broader ligand-based steering potential for optimizing activity, controlling selectivity and for providing catalytic access to new polymeric materials.

1.2.1

Ylide Nickel Complex Synthesis

Our first approach was to react a nickel(0) compound with *two* ylides, one of which was CO-stabilized [Eq. (6)].



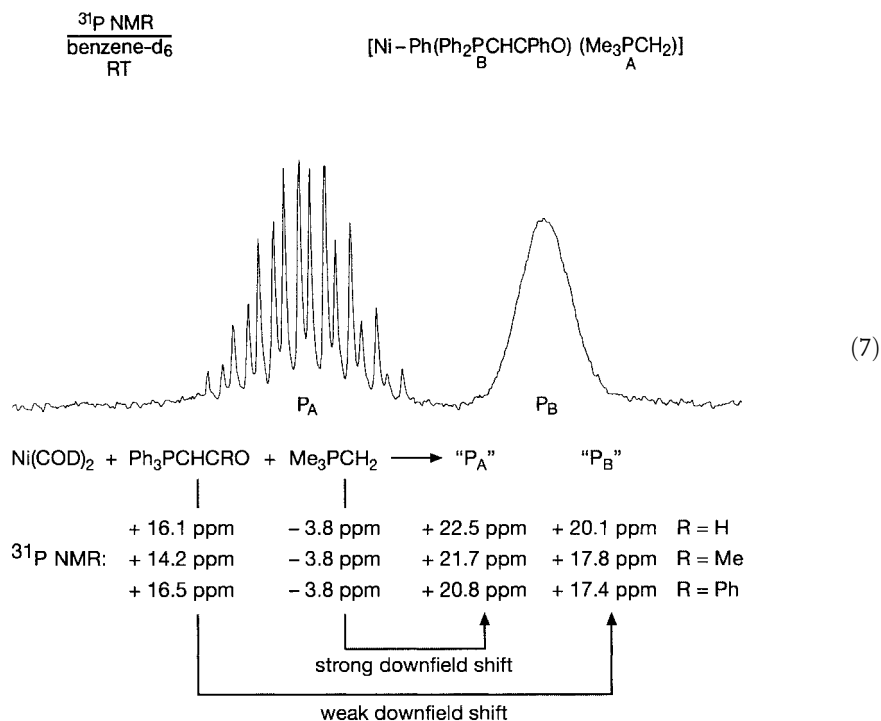
We found that the reaction of bis(cyclooctadiene)nickel(0) with the two ylides benzoylmethylene-triphenylphosphorane and methylene-trimethylphosphorane in toluene yields a highly active homogeneous catalyst (**1a**) without any co-catalyst – the ethylene turnover being approximately *tenfold* compared to **2** [10].

Complex formation takes place immediately when the methylene-trimethylphosphorane is added. A yellow solid can be crystallized from the reaction solution in high yield, microanalysis of which shows a Ni/ylide A/ylide B complex with 1/1/1 stoichiometry.

1.2.2

Spectroscopy [10–12]

Using ^{31}P NMR spectroscopy it is particularly easy to follow the reaction of the ylides **A** and **B** with the nickel(0) complex. The spectrum shows the rapid disappearance of the two ylide resonances with the simultaneous formation of two new phosphororganic moieties “ P_A ” and “ P_B ”. The reaction solution ($\text{Ni(COD)}_2/\text{Ph}_3\text{PCHCHPhO}/\text{Me}_3\text{PCH}_2/\text{toluene}$) displays the new resonances in a 1:1 ratio. A well-resolved 7 Hz doublet fine structure from $^{31}\text{P}_\text{A}-^{31}\text{P}_\text{B}$ spin-spin coupling proves that the two newly formed phosphorus groups are building blocks in a common molecular structure. The assignment is evident from the ^1H -coupled ^{31}P NMR spectrum, in which the strongly down-field shifted signal P_A of the trimethylphosphine-methylene moiety displays a characteristic multiplet splitting due to coupling with 9 equivalent H atoms from the trimethyl-P group and 2 equivalent H atoms from the P-methylene group. The slightly shifted resonance P_B of the coordinated benzoyl derivative is only broadened by ^1H -coupling [Eq. (7)].



1.2.2.1 $\text{NiPh}(\text{Ph}_2\text{PCHCPhO})(\text{Me}_3\text{PCH}_2)$ **1a**

The ${}^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1a** displays 16 C resonances, some of which are split by ${}^{31}\text{P}$ couplings, and which can be assigned to a structurally intact C-coordinated ylide ligand, a nickel-bound phenyl ligand, and a chelating bidentate (PO)-ligand.

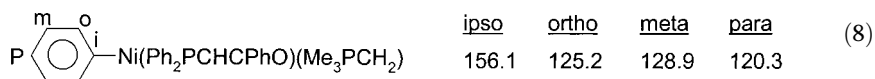
The Intact Ylide Ligand (Me_3PCH_2)

The nickel-bound anionic ylide carbon ($\delta^{13}\text{C}=7.2$ ppm) is the most strongly shielded C center of the molecule. Its position signals a negative partial charge. The four-line pattern stems from a doublet-of-doublets splitting (31 Hz/65 Hz) – the smaller coupling can be assigned to the (${}^{31}\text{P}{}^{13}\text{C}$) one-bond interaction. The size of the two-bond coupling is due to the special *trans* orientation of an ylide and a phosphane ligand in a square planar nickel coordination sphere.

In the ${}^1\text{H}$ -coupled ${}^{13}\text{C}$ NMR spectrum each of the 4 lines splits further into a 1:2:1 triplet through interaction with the two magnetically equivalent directly bound H atoms, resulting in a 12-line pattern. The 130 Hz (${}^{13}\text{C}{}^1\text{H}$) interaction indicates a pyramidalization of the anionic ylide carbon by coordination on nickel.

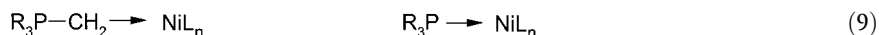
The Ni-phenyl group(Ph)

This is the other C-bound ligand. It originates from an oxidative addition of a P-phenyl moiety to nickel(0). In this way nickel binds to P and phenyl in a *cis* fashion. Accordingly, the phenyl group has a heavily deshielded ipso C atom with a two-bond *cis* coupling ${}^2J({}^{31}\text{P}{}^{13}\text{C})_{\text{cis}} = 31 \text{ Hz}$. The highfield shifts of the ortho and para C signals are indicative of a phenyl group bound to an electron-rich center (Ni). The chemical shift behavior is reminiscent of benzyl-Grignard reagents and benzyldiene phosphoranes [Eq. (8)].

**The PO Chelate Ligand ($\text{Ph}_2\text{PCHCPhO}$)**

The Ni–P complexation generates a four-coordinate phosphorus and the ligand may be viewed as a metallated ylide structure in a bis(ylide)nickel environment. The α carbon of the stabilized ylide remains trigonal planar after complexation, as indicated by the one-bond (${}^{13}\text{C}{}^1\text{H}$) coupling of 163 Hz. The double bond, which can be formulated as a phosphinoenolate structure, is strongly polarized. Owing to a partial negative charge, C- α is shifted upfield by approximately 50 ppm compared with “normal” sp^2 centers at 128 ppm. Accordingly, C- β is strongly deshielded.

The pronounced differences in the electronic structure of phosphanes R_3P and highly polar ylides R_3PCH_2 are clearly visible in valence electron photoelectron spectra (UV-PES) in that the outermost electrons of ylides (n_{C^-}) are energetically more readily available than those of corresponding phosphanes (n_{P}) (see Tab. 1.1). This feature is “sensed” by the nickel core electrons of related complexes [Eq. (9)]

**ESCA**

The ESCA (X-ray photoelectron spectroscopy) of related nickel complexes shows the $2\text{p}_{3/2}$ binding energy of the nickel center of $[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(\text{Ph}_3\text{PCH}_2)] = 853.4 \text{ eV}$ is lower than that of $[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(\text{Ph}_3\text{P})] = 854.4 \text{ eV}$ by 1 eV and thus it falls into the range of zerovalent nickel complexes! Obviously, the nickel center experiences an energetic destabilization similar to ylide C-substituents [Eq. (5)].

1.2.3

X-ray Structure Analysis [11]

The basic structure 1 is structurally related to complexes of types 2 and 3 (Tab. 1.3). A comparison is of interest because of the marked differences in activity and selectivity of ylide catalysts 1, phosphane catalysts 2, and *cis*- $[\text{Ni}(\text{PO})_2]$ bis(chelate) complexes 3. The ylide catalysts 1 are significantly more active and produce higher molecular weight products than corresponding phosphane catalysts 2. The bis(chelate) complexes 3 can be detected as polymerization-inactive decomposition products of 1 and 2, e.g. after completed oligo- or polymerization.

Tab. 1.3 Bond lengths in (PCCONi) metallocycles

Related (PO) Nickel Complexes	$d(\text{NiO})$	$(\text{CO}) [\text{\AA}]$
$[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(i\text{-Pr}_3\text{PCH}_2)]$ 1b	1.951	1.302
$[\text{NiPh}(\text{Ph}_2\text{PCHCPhO})(\text{PPh}_3)]$ 2	1.914	1.313
$[\text{Ni}(\text{Ph}_2\text{PCHCPhO})_2]$ 3	1.885	1.318

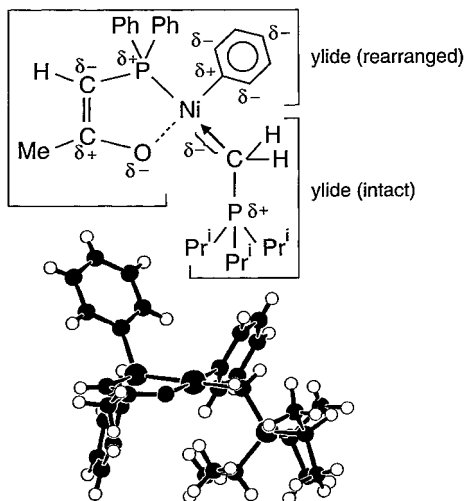


Fig. 1.2 X-ray structure and charge distribution of the bis(ylide)nickel catalyst $[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(i\text{-Pr}_3\text{PCH}_2)]$.

An X-ray structure determination of $[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(i\text{-Pr}_3\text{PCH}_2)]$ (Fig. 1.2) confirms the presence of a structurally intact C-coordinated $i\text{-Pr}_3\text{PCH}_2$ -ylide ligand in the *trans* position to the diphenylphosphino group of a $\text{Ph}_2\text{PCHCMeO}$ -PO chelate. The most striking finding is a dramatic increase in the Ni–O bond length to 1.95 Å as a consequence of a structurally intact coordinated ylide ligand (Tab. 1.3). The stepwise weakening of the Ni–O bond correlates with enhanced catalyst activity.

In summary, prominent features of ylide nickel complexes versus phosphane complexes have been identified: an electron-rich nickel center, energetically destabilized nickel-localized occupied orbitals, a significant weakening of the Ni–O bond, the phosphorus moiety being located outside the nickel coordination plane, thus opening one axial position in the nickel coordination sphere for easy monomer “landing”.

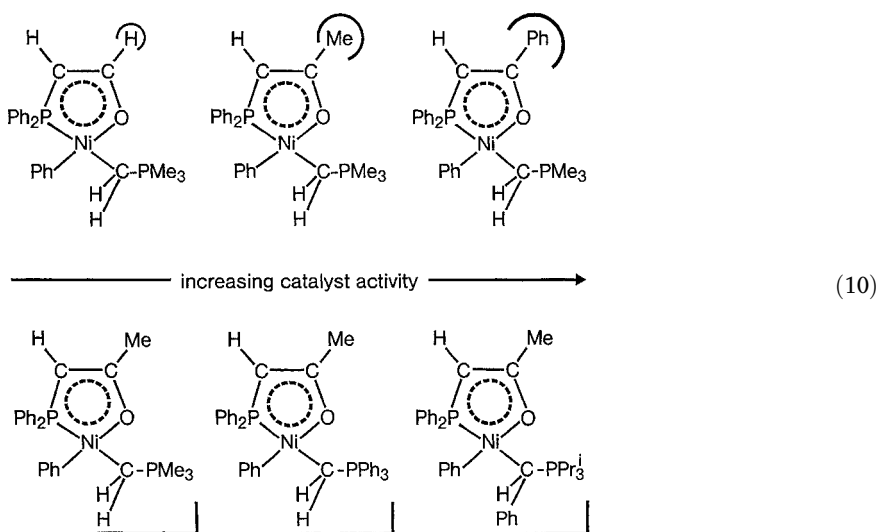
1.3

Ethylene Polymerization

1.3.1

Catalyst Activity [10, 12, 13]

Different ligand properties affect the homogeneously catalyzed oligo-/polymerization of ethylene. The nickel catalysts with structurally intact ylide ligands have considerably higher activities than comparable nickel phosphane systems. The Me_3P -nickel complex is even catalytically inactive. Frontier orbitals, as well as activity of the catalysts are influenced by variations of the intact ylide ligand. Interestingly, when the chelating acetylmethylene-triphenylphosphorane is kept unchanged, the turnover increases with decreasing first ionization potential of the structurally intact coordinating ylides [Eq. (10), bottom].



Likewise, the phosphorus-31 coordination chemical shift ($\Delta\delta\text{P reori/coord}$) of the chelate-phosphorus reflects the properties of the intact steering ligand which are transmitted by the nickel into the metallocycle. The “intact ylide”-dependent chemical shift behavior is mirrored in the activity profile of the catalyst system [12].

When, on the other hand, the intact ylide ligand Me_3PCH_2 is retained [Eq. (10), top], the turnover increases in the sequence formyl-, acetyl-, benzoyl-methylene-triphenylphosphorane, at 10 bar and approximately 100°C , to around 0.5×10^5 mole reacted ethene per mole nickel per hour. This corresponds to a catalyst activity of 1.4×10^6 g PE or 1.4 tons PE produced per mole of catalyst without using any co-catalyst or noncoordinating anions.

1.3.2

Novel Ligand Control of PE Molecular Weight [13]

GC analyses of the reaction solutions show the formation of the homologous series of ethene oligomers butene, hexene, octene, decene, etc. While the phosphane-induced Schulz-Flory distributions fall off rapidly, the ylide-derived catalysts favor formation of higher oligomers. Oligomers above C_{40} are detectable. Both ylide ligands affect the ratio of the reaction rates propagation/termination. The quotient of the corresponding rate constants can be derived from neighboring GC peaks.

The intrinsic viscosities of the solid oligo-/polyethenes from ylide-steered nickel-catalyzed polymerizations are higher than those produced by related Ni-phosphane systems. Provided the polymer structure remains unchanged, the “Ni-ylide-steered” products consist of longer macromolecules and, accordingly, have higher molecular weights. IR data show correspondingly fewer end groups (methyl or vinyl) per 1000 C. The DSC curves of the low-melting “Ni-phosphane-steered” oligoethenes are contrasted by higher melt temperatures in ylide catalysis. GPC investigations confirm the expected higher molecular weights for the ylide-derived products.

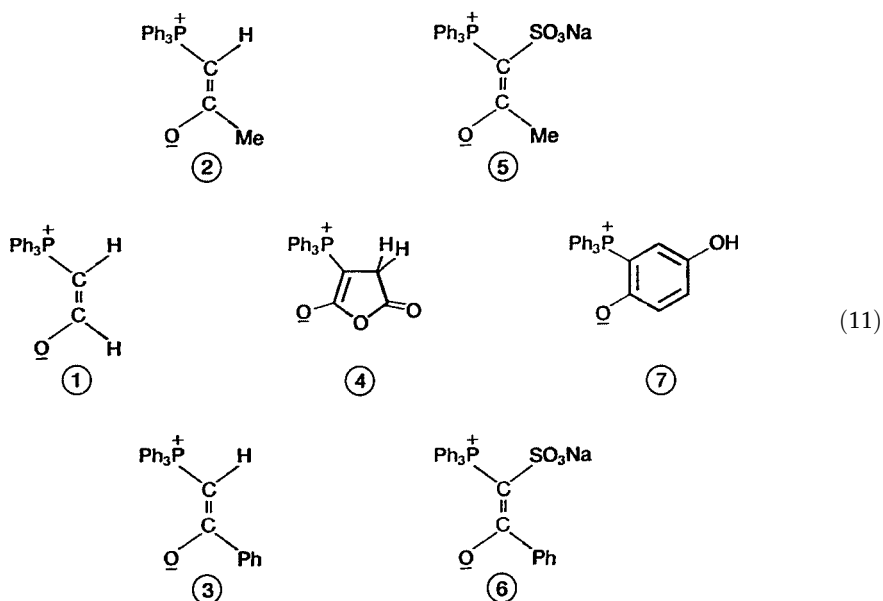
In the above-mentioned bis(ylide)nickel series [Eq. (10), top], where the intact ylide ligand Me_3PCH_2 is kept constant and the PO component is changed at the β -position from $H \rightarrow Me \rightarrow Ph$, substituting the formyl-methylenephosphorane at the β -position with a methyl group (hyperconjugation in acetyl-methylenephosphorane) affects the catalytic cycle with respect to turnover and polymer properties; the effect is even greater for substitution by a phenyl group (π -conjugation in benzoyl-methylenephosphorane). The catalyst activity increases – and so does the intrinsic viscosity of the PE formed, from approximately 0.05 to approximately 0.13 dL g^{-1} . Chain propagation as opposed to chain termination and chain transfer are favored by the ligand field modifications.

We therefore looked for other ($R_3P-C=C-O$) components in the (ylide A/ylide B/Ni) concept that would allow us to control the molecular weight to a greater extent.

Indeed, more marked chemical changes in the PO component dramatically altered the selectivity for the PE molecular weight and led to a *novel* ligand-steered molecular weight control. The molecular weight increases in the ligand series $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 6 \rightarrow 7$ [Eq. (11)].

A sulfonate substituent at the α -position results in high molecular weight PEs. The already mentioned β -substituent effects on the PE molecular weight can be detected here again, i.e. the sulfonated benzoyl derivative exceeds the acetyl derivative. Incorporating the α - and the β -carbon into a ring system also increases the molecular weight, with phosphane-chinone adducts being at the top of the scale.

An extreme range of high to ultra-high molecular weight PE is accessible by using an in-situ catalyst, obtainable by reacting 1 mmol of each of the three components $Ni(COD)_2/Ph_3P$ -benzochinone/ Ph_3PCH_2 in 10 ml toluene at 50 C for 2 hours. The heterogeneous reaction mixture catalyzes the polymerization of ethyl-



ene for example in cyclohexane at 10 bar and polymerization temperatures between 10 C and 150 C. The intrinsic viscosities measured in o-dichlorobenzene at 140 C and therefrom calculated viscosity average PE molecular weights depend strongly on the polymerization temperature.

150 C PE sample	0.89 dl/g	44 000 g/mol
130 C PE sample	1.53 dl/g	97 000 g/mol
110 C PE sample	3.60 dl/g	328 000 g/mol
90 C PE sample	5.65 dl/g	624 000 g/mol
70 C PE sample	9.12 dl/g	1 237 000 g/mol
50 C PE sample	10.01 dl/g	1 412 000 g/mol
30 C PE sample	12.62 dl/g	1 965 000 g/mol
20 C PE sample	13.27 dl/g	2 112 000 g/mol
10 C PE sample	14.19 dl/g	2 324 000 g/mol

High temperature GPC studies show that the 20 C PE sample is monomodal and has a narrow molecular weight distribution. The polydispersity M_w/M_n of 2.4 indicates a single site insertion mechanism. With increasing polymerization temperature the molecular weight distribution broadens.

Further chemical fine tuning has been achieved by means of additional ligands with ylide-type bond systems from the iso-electronic series of highly polar P-ylides, P-imines and P-oxides. Examples for HDPEs (high density polyethylenes) are given in Tab. 1.4.

No oligomers are detectable in solution. Some of the very high molecular weight polymers show long chain branching. This observation may indicate that part of the molecular weight build-up may originate from reincorporation of vinyl-

Tab. 1.4 Polyethylene properties obtained with [Ni/Ph₃P-BC/R₃PX] catalysts

<i>In situ</i> catalyst: Ni(COD)₂ Ph₃P-BC	T_p [°C]	η [dL g ⁻¹]	ρ [g cm ⁻³]
Ph ₃ PO	65–85	9.60	0.968
(PhO) ₃ PO	60–100	5.85	0.960
Me ₃ PO	75–80	4.29	0.968
(Me ₂ N) ₃ PO	90	2.43	0.972
(MeO) ₃ PO	90–100	1.40	0.969

Abbreviations used: *in situ* catalyst: 2 mmol of each component preformed for 1 h at 50 °C; Ni(COD)₂: bis(cyclooctadiene)nickel(0); Ph₃P-BC: 1/1 adduct of triphenylphosphane and *p*-benzochinone; Me: methyl; Ph: phenyl; T_p : polymerization temperature; T_m : melt temperature (DSC); η : intrinsic viscosity, measured in tetraline at 140 °C; ρ : PE density. Polymerization conditions: *in situ* catalyst in 50 mL toluene, solvent: cyclohexane, ethylene pressure: 100 bar.

terminated high molecular weight PE chains. High density polyethylenes are usually unbranched and characterized by a density $\rho = 0.96\text{--}0.97\text{ g cm}^{-3}$.

An outstanding property is the systems tolerance towards solvents of different polarity with respect to maintaining catalyst activity, while at the same time creating an additional tool to control molecular weight. Increasing polarity results in reduced molecular weight. Thus, nickel catalysts with ylide ligands have for the first time opened access to all molecular weight ranges up to 10^6 g mol^{-1} and above; from ethene oligomers to polymers – from liquid α -olefins to soft and hard waxes and further up to HDPE and even ultrahigh molecular weight polyethylene (UHMW PE) with DSC melt temperatures up to 137 °C.

1.3.3

Linear and Branched Macromolecules [14]

“Tailor-made materials” require access to linear as well as to branched macromolecular structures. FTIR spectra of the polymer and GC analysis of the oligomers in solution (if present) can be used for characterization and as a reference for structural changes.

1.3.3.1 Linear Macromolecules

The selectivity of the bis(ylide)nickel catalysts frequently favors the formation of linear macromolecules with unsaturated end groups. In this case the FTIR spectrum of a PE film of defined thickness shows almost exclusively methyl and vinyl end groups. Their presence in equal quantities proves linearity. An example for the catalytically controlled formation of linear, unbranched macromolecules is given in Eq. (12).

[NiPh(Ph ₂ PCHCMeO)(Pr ₃ PCHPh)]	12	vinyl per 1000 C	(12)
	0.2	vinylidene per 1000 C	
	0.4	trans-vinylene per 1000 C	
	12	methyl per 1000 C	

A mean degree of polymerization of 42 and a molecular weight M_n of approximately 1200 g mol⁻¹ can be estimated from the quantitative end group determination in the given example.

Gas chromatographic analysis identifies the oligomers in the reaction solution as an homologous series of linear α -olefins in the range C₄ to C₄₀.

1.3.3.2 Short Chain-Branched Macromolecules

A conventional approach to the controlled formation of short-chain branches is ethene copolymerization with co-monomers such as propene, butene(1), 4-methylpentene(1), hexene(1) or octene(1). In the ethene/propene copolymerization example given below an increased number of methyl groups compared with vinyl end groups is consistent with a propene incorporation of approximately 6 mol% [Eq. (13)], the observed lower DSC melt temperatures and lower densities are typical for medium density (MDPE) and linear low density polyethylene (LLDPE).

Ni(0)/Ph ₃ PC(SO ₃ Na)CPhO/Ph ₃ PCHCHCHPh	6	vinyl per 1000 C	(13)
	0.2	vinylidene per 1000 C	
	0.4	trans-vinylene per 1000 C	
	35	methyl per 1000 C	

Ylide nickel-catalyzed ethylene polymerizations can also produce branched macromolecules from ethylene alone (that is *without* adding a co-monomer) due to ligand effects, which induce a nonlinear specificity. This “self-branching” can be achieved with special ylide ligand combinations and adequate reaction conditions, which allow the insertion of olefins other than ethylene into Ni–H and/or Ni–C bonds. Low ethylene pressure and high catalyst concentrations favor self-branching. With the catalyst shown in Eq. (14), almost equal quantities of vinylidene, *trans*-vinylene and vinyl double bonds are formed. The excess methyl content versus the total number of double bonds per 1000 carbon atoms, and the appearance of significant amounts of vinylidene groups, indicate a branched structure.

Ni(0)/Ph ₃ PC(CMeO) ₂ /Ph ₃ PCH ₂	9	vinyl per 1000 C	(14)
	9	vinylidene per 1000 C	
	9	trans-vinylene per 1000 C	
	57	methyl per 1000 C	

The appearance of *vinylidene* double bonds may be interpreted by successive chain growth, chain termination by β -H elimination with formation of α -olefin,

then start of a new chain by insertion of ethylene into Ni–H, growing of the new chain by migratory insertion of ethylene into the Ni–C bond, followed by 1,2-reinsertion of a preformed α -olefin after one or more ethylene insertions with subsequent loss of vinylidene-terminated chain via β -H elimination. The appearance of internal *vinylene* double bonds hints at cascades of reversible elementary steps of the type β -H elimination and readdition of the Ni–H complex to the thereby formed double bond. The fact that the Ni–H can add in both directions to the double bond leads to a random movement of the metal along the macromolecule (so-called chain walking [14c]). Whenever an ethylene inserts into a Ni–C bond of a secondary (internal) carbon atom it generates a branching point. *Vinylene* double bonds can in principle also originate from a less favorable 2,1-reinsertion of an α -olefin with subsequent chain termination.

1.3.3.3 Long Chain-Branched Macromolecules [14]

LCB-PE (long chain branched polyethylene) is not accessible through simple ethylene/ α -olefin copolymerization. Therefore, a bifunctional bimetallic catalyst was developed, in which one active center oligomerizes ethene to long-chain α -olefins, while the other copolymerizes them with ethene.

Homogeneous ylide-nickel systems were combined with heterogeneous surface chromium(II) catalysts. Both separate catalyst systems work in the absence of aluminum alkyl co-catalysts. In this process the nickel complex is supported on the chromium contact, resulting in a new heterogeneous catalyst, which is active in the ethylene polymerization and where two different catalytic centers “co-operate” [14a, b].

Polymer analytical, spectroscopic and rheological data, compared with those of linear HDPE produced with a surface Cr(II)/silica catalyst, strongly suggest that the bifunctionally produced polyethene (BiPE) has a long chain-branched structure.

Other catalytic systems that generate long chain-branched polyolefins have been reported such as Dow's half-sandwich constrained geometry titanium catalysts (CGC) [14e], and Bayer's novel donor/acceptor metallocenes [14f]. This polymer structural feature improves material and processing properties.

1.3.4

Styryl-Terminated Oligo-/Polyethylenes [15]

The ylide nickel-catalyzed oligo-/polymerization of ethylene in the presence of styrene or substituted styrenes with unpolar or polar substituents results predominantly in styrene-terminated oligo-/polyethylenes. Usually, no styrene homopolymerization takes place. The ethylene pressure has to be adjusted relative to the styrene concentration to reduce the competing formation of simple α -olefins. High styrene concentration and low ethylene pressure favor homologous series of the composition $\text{aryl-C}_m\text{H}_{2m-1}$. While the aryl group is frequently located at one

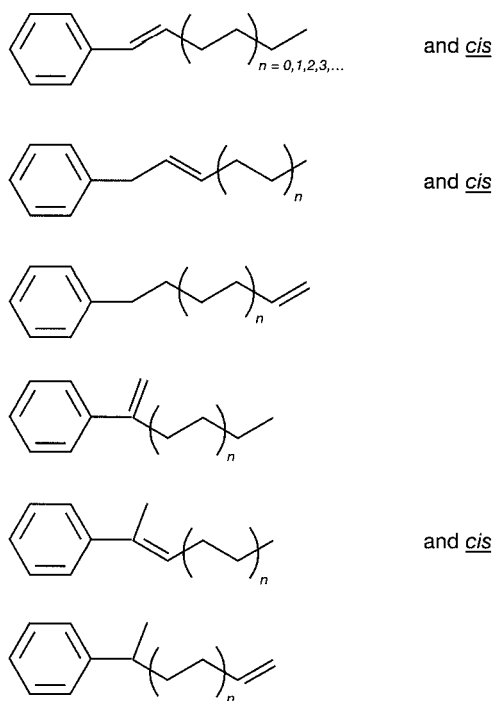


Fig. 1.3 Homologous series of isomers from the ylide nickel-catalyzed reaction of ethylene and styrene.

end of the unsaturated hydrocarbon chain, the double bond may or may not be in conjugation with the aromatic ring. A detailed GC/IR- and GC/MS-analysis reveals several isomeric homologous series, in each of which the double is located in a different position (Fig. 1.3). In one homologous series the double bond is in conjugation with the aromatic ring, in others it is somewhere along the chain, and in yet another series it appears at the chain end opposite the aryl group.

Furthermore, vinylidene groups are detectable adjacent to the aryl group. This manifold of an isomeric homologous series gives insights into the operative catalytic mechanisms: the aryl group with a conjugated double bond appears when the styrene monomer inserts in a 2,1-fashion into the Ni–C bond of the growing polyethylene chain, followed by β -H elimination. Accordingly, when the 1,2-insertion product terminates the chain by β -H elimination it generates vinylidene groups. Internal double bonds are generated by chain walking. Terminal double bonds are best explained as originating from a styrene insertion into the Ni–H species, followed by a number of ethylene insertions and chain termination by β -H elimination. The logic behind these deductions is comparable to that in the discussion on the origin of the self-branching ethylene polymerizations.

The described novel synthetic process opens the way to a large number of new macromonomers. Of especially high interest are those derived from polar or unpolar substituted styrenes and such where the substituent is a reactive group. One prominent example is divinylbenzene (DVB), which, when catalytically converted

with ethylene, yields oligo-/polyethylenes, each chain with a highly reactive styryl end group and a less reactive double bond in the chain. These styrenic macromers can for example be copolymerized with other monomers using radical or anionic initiators to create a whole array of new polymeric materials with interesting properties.

1.4

Cycloolefin Polymerization [16, 17]

Cycloolefins such as norbornene can be polymerized with high efficiency (e.g. 18.6 tons (mol $[\text{NiPh}(\text{Ph}_2\text{PCHCPhO})(\text{Pr}_3\text{PCHPh})]^{-1} \text{ h}^{-1}$) when the nickel catalysts are used in combination with aluminoxanes such as MAO. The polynorbornenes typically obtained are high molecular weight amorphous thermoplasts with very high T_g values and decomposition temperatures as high as 450–464 °C. Softening points vary between ca. 280 and 400 °C and the polymers are soluble in chlorobenzene. The situation changes when ylide palladium catalysts are used. Owing to different microstructures the polymers become insoluble. However, the softening temperature drops to ca. 250 °C.

1.5

Butadiene Polymerization [18]

Ylide nickel catalysts can be activated with aluminum co-catalysts such as ethylaluminum chloride to oligomerize butadiene to low molecular weight oils. When the catalyst is modified with boron trifluoride it produces high molecular weight polybutadiene rubber. The butadiene units are linked predominantly (95–99%) in a 1,4-fashion. Only 1–5% of the butadiene molecules are incorporated in a 1,2-fashion, which create daugling vinyl Substituents on the polybutadiene main chain. The configuration at the double bonds is medium to high *cis* (45–85%); – i.e. 45–85% of the double bonds along the chain are *cis*-configured the others are *trans*-configured.

1.6

Polar Monomer Polymerization [19]

The high polar group tolerance of co-catalyst-free ylide nickel catalysts makes them interesting candidates for the polymerization of polar monomers. In fact, quite a number of polar vinyl monomers can be homo- and copolymerized quite effectively. The mechanisms of initiation and chain propagation have not been elucidated yet. Especially, acrylic monomers are well suited. It is thus possible to produce, for example, poly(methyl methacrylate), poly(ethyl acrylate) and poly(butyl acrylate) in high yield [Eq. (15)].

monomer	1 mol	$\text{H}_2\text{C}=\text{CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OC}_4\text{H}_9$	
catalyst	1 mmol	$[\text{NiPh}(\text{Ph}_2\text{PCHCMeO})(\text{Pr}_3^i\text{PCHPh})]$	
temperature	at ~ 40°C strongly exothermal, temperature rises above 140°C		(15)
polymer yield	41% poly(butyl acrylate), determined after 3 h		
intrinsic viscosity	$\eta = 0.54 \text{ dl/g}$, in tetrahydrofuran at 25°C		

The molecular weights achievable, with proper temperature control, are high ($M_w \geq 10^5 \text{ g/mol}$) to ultrahigh ($M_w \geq 10^6 \text{ g/mol}$), the polydispersities are narrow ($M_w/M_n = 2-3$) to medium ($M_w/M_n = 4-6$). Using this type of ylide nickel catalysis it is possible to synthesize interesting copolymers, such as the 2-ethylhexylacrylate-glycidylmethacrylate copolymer, which is a vulcanizable rubber with excellent low-temperature properties.

With $[\text{NiPh}(\text{Ph}_2\text{PCHCPhO})(\text{Pr}_3^i\text{PCHPh})]$ applied at a polymerization temperature of 80 °C in bulk polymerization, a copolymer with a molecular weight $M_w = 681 \text{ kg mol}^{-1}$ and a polydispersity of 3.8 has been obtained in high yield. The glass transition temperature T_g was determined by DSC to be -67 °C.

1.7

Acetylene Polymerization

Catalysis research by Reppe et al. (1948) and Natta et al. (1958) initiated the search for a new material: polyacetylene. It stimulated tremendous research effort worldwide, especially over the past two decades. Unlike contemporary developments for polyethylene and polypropylene, polyacetylene has yet to become a useful product.

The original material (subsequently called URPAC) is accessible in various morphologies with a large number of Ziegler-Natta type and other transition metal catalysts. It has been studied in detail with spectroscopic and other physico-chemical methods. Quantum theoretical model calculations have provided insights into the energetics of conjugated double bond systems.

Material science interest focuses on potential applications of its specific electronic and band structure. Metal-like conductivities, semiconductor properties, photoconductivity and the nonlinear optical features of URPAC samples suggest devices for electromagnetic shielding, energy storage, microelectronics, optoelectronic and optooptical communication or optical computing.

However, URPAC is a *black, insoluble, infusible* material which cannot be processed. The 3-dimensional crosslinking not only hinders the analytical polymer characterization. In addition, owing to the resulting lack of synthetic/catalytic

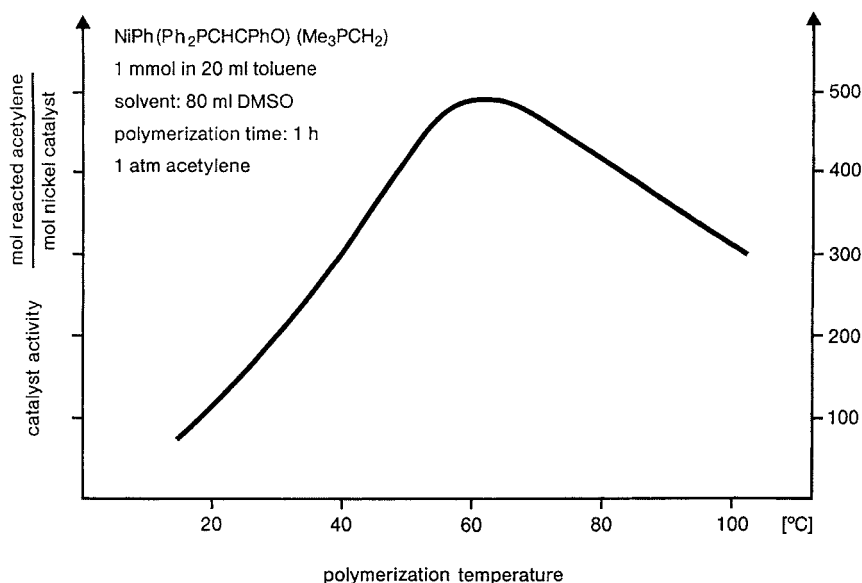


Fig. 1.4 Temperature dependence of the ylide-Ni catalyst activity in acetylene polymerization.

control over the (unknown) polymer architecture, an application-oriented product optimization becomes difficult. To make matters even worse, URPAC is unstable in air and thus, up to now, virtually useless.

Clearly, novel concepts for catalysts, changing the property profile, had to be developed to overcome these drawbacks.

1.7.1

Catalyst Activity [20]

Bis(ylide)nickel catalysts are of high chemical variability and show superior performance in the activation of unsaturated substrates such as acetylene. The normalized polymerization activity in dimethyl sulfoxide (DMSO) of 500 mol polymerized acetylene per mol nickel $(\text{h atm})^{-1}$ by far exceeds that of structurally related phosphane catalysts by a similar order of magnitude as observed in ethylene polymerizations (see Sections 1.2 and 1.3.1). To our knowledge this activity even exceeds that of all other nickel catalysts reported so far (Fig. 1.4).

1.7.2

MATPAC, Novel Highly Polar Matrix Polyacetylenes [21, 22]

The high polar group tolerance of ylide nickel catalysts enables the polymerization of acetylene in polymer solutions not only of low polarity but also of medium and high polarity. These options provide synthetic access to a wide range of novel matrix polyacetylenes (MATPAC). Examples of polymers that may be used as matrix

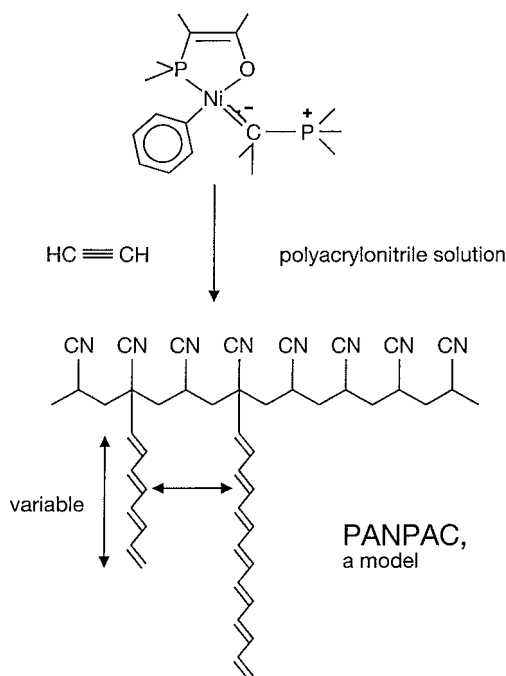


Fig. 1.5 PANPAC, model of a novel matrix polyacetylene.

polymers are polyethylene, polypropylene, polystyrene, polyisoprene, polychloroprene, poly(vinyl chloride), polycarbonate, polyvinylpyrrolidone, polyvinylcarbazole, poly(ethyl acrylate), poly(methyl methacrylate) and methylated cellulose.

Some of the innovative materials contain PAC in a highly dispersed heterogeneous distribution. Others are homogeneous and soluble. All of them can be processed by conventional techniques such as melt and blow extrusion, fiber spinning, film casting or spin coating. And some of them even provide the necessary matrix stabilization for turning polyacetylene into a useful material.

Homogeneous types of MATPAC are of special importance. They are based on highly polar matrix polymers and are soluble in equally polar solvents. They successfully prevent the 3-dimensional crosslinking, allow processibility and the buildup of highly ordered structures, and last-but-not-least stabilize PAC against oxidation.

Yellow, orange, red, violet and blue, and thus the distribution of conjugation lengths, can be adjusted by using different catalysts at various polymerization temperatures. Several ligand effects that were already shown to control the molecular weight in ethylene oligo-/polymerizations are again operative in acetylene polymerization in determining the length of the polyacetylene chains. A well-studied example is PANPAC (Fig. 1.5), a polyacetylene based on polyacrylonitrile, which is soluble, for example, in dimethylformamide (DMF).

It can be precipitated from and redissolved in DMF or DMSO and processed, e.g., into fibers. PANPAC with up to and above 70 mol% (!) of solubilized PAC has been prepared by polymerizing acetylene in polyacrylonitrile/DMF solution

using bis(ylide)nickel catalysts. The polyacetylene concentration in the polymer matrix is determined by the amount of catalyst used and by the polymerization time (Figs. 1.6–1.8).

The results are consistent with a model of polyacetylene sidechains on the matrix polymer backbone. While the mechanistic origin of the proposed graft reaction is unknown, a CH activation of a bond geminal to the polar substituent could explain the range of polymers accessible by this novel synthetic route.

Other polymers which also contain acrylonitrile units, such as styrene–acrylonitrile copolymers, are useful matrices. The latter solutions have an opaque appearance which hints at a different folding and association/micelle-forming behavior. The solid SANPAC can be readily melt extruded at 235 °C into shining black profiles of long term stability.

1.7.3

POLPAC®, a Tailor-made Polyacetylene Application [23]

In their extraordinary tolerance for polar functional groups ylides/nickel catalysts offer yet another synthetic highlight as they allow for the preparation of poly(vinyl alcohol)-based polyacetylenes. Water-soluble (!) PVAPACs of different color and composition can be processed into films of any desired thickness. The highly polar matrix protects the polyacetylene chains against oxidative attack and crosslinking. Furthermore, it offers the option of attaining high degrees of order through a drawing process.

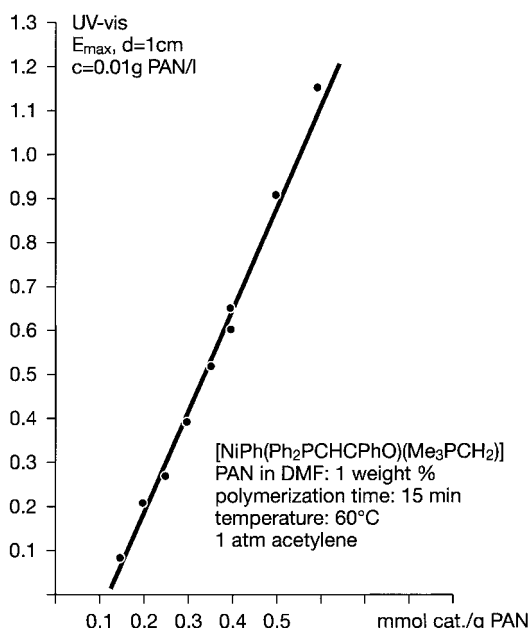


Fig. 1.6 UV/vis absorbance of PANPAC as a function of catalyst concentration.

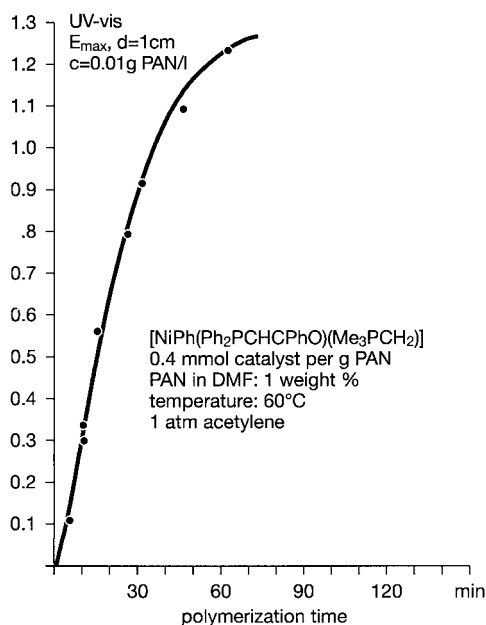


Fig. 1.7 UV/vis absorbance of PANPAC as a function of polymerization time.

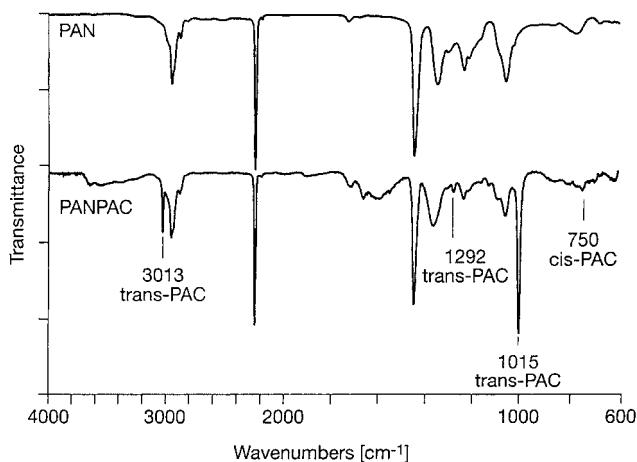


Fig. 1.8 FT-IR spectrum of a PANPAC, containing 32 mol% acetylene; the polyacetylene segments contain ca. 95% *trans* configuration (bottom); PAN (top).

Stretch-oriented poly(vinyl alcohol) films which contain iodine are essential light polarizing components in today's liquid crystal displays (LCDs). They do, however, suffer from the inherent diffusion and sublimation problems of iodine and its chemical aggressiveness. The latter also prevents realization of new LCD

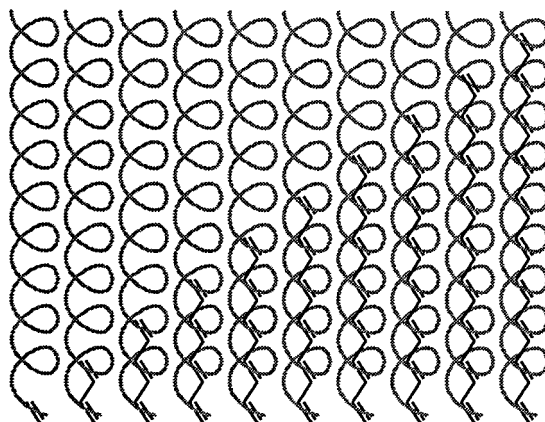


Fig. 1.9 POLPAC, model for a novel linear polarizer based on polyacetylene.

construction principles. PVAPAC provides an all-polymer high-tech material alternative (Fig. 1.9).

The excellent catalytic control in the process of synthesizing PVAPAC allows the use of the molecular energy levels and symmetry of quasilinear highly conjugated π -systems in tailoring the macroscopic properties for LCD applications. Catalysts that cause selfbranching are not useful for this purpose. An assembly of linear polyenes can be synthesized in the acetylene polymerization, whose integral spectral absorption curve extends over the whole visible light region (450–680 nm), being optimized to fit the human eye sensitivity curve and the intensity of the LCD light source. The polymer can be processed into thin films of precise thickness. By stretch-orienting the film uniaxially, the chromophores have to be arranged in a completely parallel fashion. When visible light passes through this film, the electromagnetic radiation that vibrates within the direction of the polyacetylene chains is absorbed, while the perpendicular component of light passes through unhindered, rendering the transmitted light linearly polarized.

When PVAPAC films, optimized with respect to conjugation length distribution and PAC concentration, are stretched in a controlled manner they turn into highly dichroic transparent neutral grey POLPAC® filters (Fig. 1.10). The absence of coloration is indicative of an exceptionally highly ordered PAC state in these novel all polymer broadband polarizers based on polyacetylene (POLPAC®).

1.7.4

MATPAC for NLO Devices [24]

Another inherent property of polyacetylene chains, associated with the highly delocalized π -system, is the polarizability in an electromagnetic field. The dipole moment induced by the oscillating electric field of electromagnetic radiation may be expressed as the sum of the linear polarizability and nonlinear higher terms (hy-

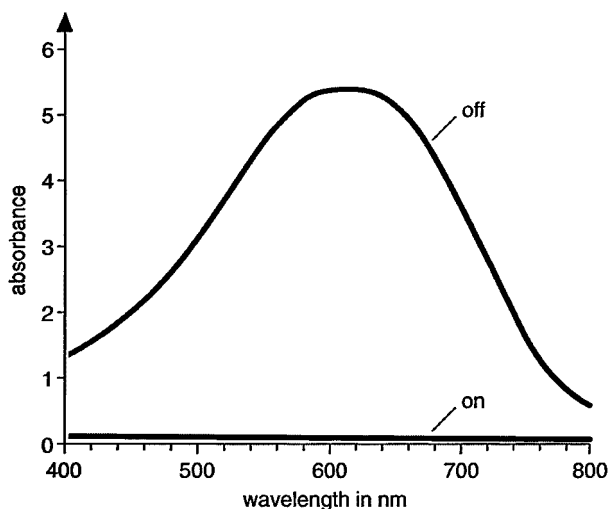


Fig. 1.10 POLPAC: on/off-state absorbances for polarized light.

perpolarizabilities). On the macroscopic level the corresponding terms are the susceptibilities. The third order susceptibility $\chi^{(3)}$ gives rise to an intensity-dependent nonlinear refractive index. This material property will become increasingly important in the upcoming “information age”. Electronics will be substituted by photonics in order to save time and energy. Copper wires will be substituted by optical fibers, electrical signals by optical signals, and transistors by nonlinear optical (NLO) devices. Large amounts of these devices will be needed for optical communication. NLO polymers are thus needed to control the propagating properties of light, polymers that have high NLO effects, high stability, easy processibility and low material costs.

Therefore, the so-far developed catalytic instruments were tested within this focus of advanced material properties. A series of different MATPAC polymers of different color were synthesized with different catalysts and the $\chi^{(3)}$ values determined in solution. A blue PVAPAC solution with an absorption maximum at 650 nm exhibited an excellent third order susceptibility $\chi^{(3)}$ of 2.1×10^{-13} normalized to 1 g PAC per liter of solution.

1.8

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2

Microstructure Control of Ethene Homopolymers Through Tailored Ni,Pd(II) Catalysts

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2.1

Introduction

The development of early transition metal complexes as catalysts for olefin polymerization marked a breakthrough in the history of metal-catalyzed insertion reactions [1]. In contrast to heterogeneous Ziegler-Natta systems, these homogeneous catalysts are structurally well-defined compounds granting mechanistic investigations on a molecular scale. Intensive research on versatile, new catalyst architectures enabled scientists to adjust polymer properties precisely suited to users need. However, the strongly oxophilic behavior of early transition metals limits the portfolio of utilizable monomers. This major drawback is clearly exposed in the presence of olefins bearing polar functionalities that irreversibly induce blocking of the catalytic center [2, 3]. Nonetheless, copolymers of ethene and acrylic monomers are of industrial interest and successfully have found access into the polymer market. These materials are usually prepared by free radical polymerization processes [4]. Propene as one of the most important monomers in industry, however, forms under radical conditions only oligomers which prevents the production of high-molecular weight copolymers [5]. Only by additional grafting reactions of acrylates on isotactic polymers are polar modified polyolefins available.

Nowadays, catalysts on the basis of late transition metals are pushing to the fore as alternative compounds assisting the way to copolymers of apolar and polar olefins. These compounds are less oxophilic, display a higher tolerance towards polar functionalities and have recently indicated their potential to provide control for the regioregular, alternating copolymerization of olefins with CO [6]. Since the 1970s alkyl compounds of late transition metals have been known for their ability in the insertion polymerization of acrylic acid derivatives [7]. Yamamoto et al. successfully introduced bipyridine-coordinated iron and cobalt alkyl complexes for the homopolymerization of acrylonitrile (Fig. 2.1, A). Unfortunately, these complexes suffered a weak coordination of the bipyridyl ligand which facilitates β -H migration and reductive elimination of the growing polymer chain leading, consequently, to rapid deactivation of the catalytically active species [8].

Despite the major disadvantage of reduced activity in olefin insertion reactions, late transition metals remarkably marched into the sophisticated field of industrially

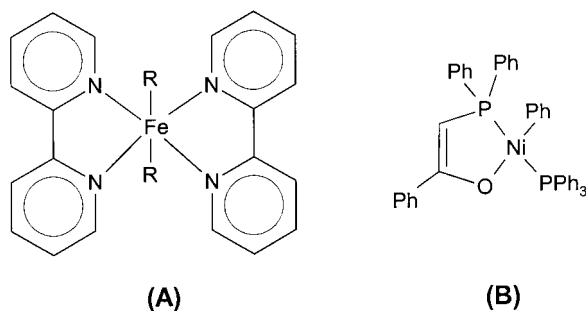


Fig. 2.1 Bipyridine-coordinated iron alkyl complex **(A)** for the polymerization of acetoni-

trile (Yamamoto et al.). **(B)**: P∩O complex for ethene oligomerization (Keim et al.).

relevant source materials for polymerization catalysis. The commercially significant Shell Higher Olefin Process (SHOP) takes advantage of the competing β -H elimination and the facile-associative olefin exchange reactions which occur during the polymerization process and often lead to dimers or oligomeric products [9]. For that reason, SHOP is the first choice in the design of linear α -olefins (C_4 – C_{20}) which are commonly used for detergents, plasticizers, lubricants and a variety of fine chemicals [10]. This capability spurred scientists to expend fundamental research in the design of a variety of new late transition metal catalysts. The development, therein, was started in the late 1960s to early 1970s by Keim et al. (Fig. 2.1, B) [11] who finally found the first defined complex providing the formation of α -olefins and polyethene without the use of a co-catalyst by conversion of bis(cyclooctadienyl)nickel, phosphorane and triphenylphosphine [10]. Treatment of a toluene solution of the Ni–P∩O complexes with ethene afforded activities up to 6000 mol ethene per mol of the catalyst and formed linear products (99%) with an α -olefins content of 98%. Replacement of toluene with *n*-hexane formed high molecular weight linear polyethene. The significance of these results is manifested in the high scientific interest which was increasingly centered on detailed mechanistic investigations [12, 13]. Keim et al. identified that a nickel hydride compound operates as the active catalyst species in nickel-catalyzed oligo- and polymerizations reactions (Fig. 2.2). An ethene molecule is inserted in the Ni–H bond, resulting in the formation of a nickel ethyl unit. Further insertions of monomer in the nickel-alkyl bond and subsequent β -H elimination produce linear α -olefins with high selectivity.

The chemical modification of SHOP-catalysts was the center of interest of Kläbunde and Ittel who intensively focused on the synthesis of high molecular weight products and on the copolymerization of ethene with α -olefins. Therein, the combination of ethene with polar monomers and carbon monoxide depicts the major concern [14]. They realized the importance of the nature of donor ligands coordinating to the nickel center as the primary factor limiting the polymer molecular weight (Fig. 2.3, C).

A first approach aimed at removing the defective, strong donor ligands (for example PPh_3) from the coordination sphere was the addition of catalyst promoters

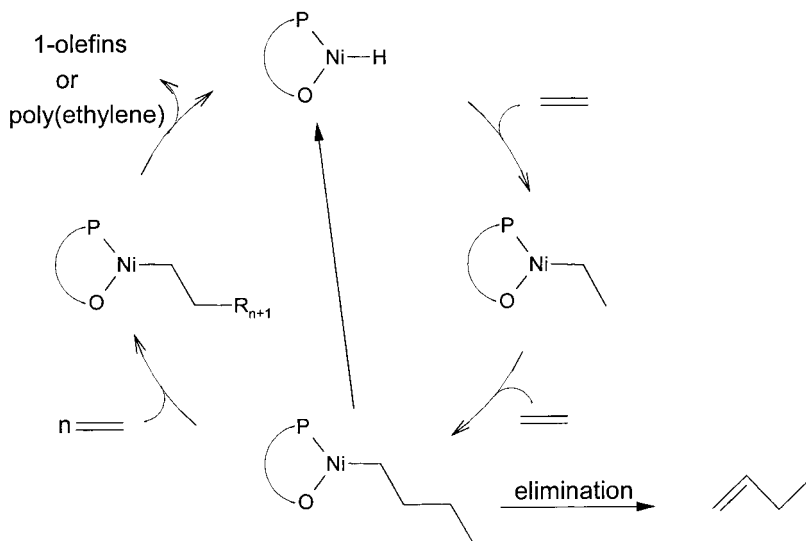


Fig. 2.2 Postulated mechanism for the Shell Higher Olefin Process (SHOP).

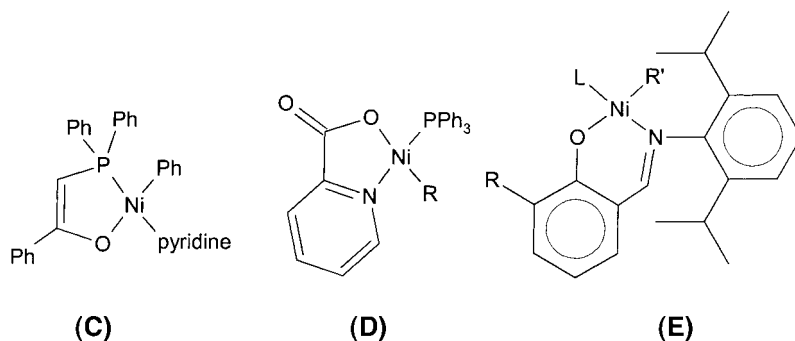


Fig. 2.3 Weakly coordinated pyridine (C) provides access to higher molecular weight products (Klabunde, Ittel et al.). (D) Neutral Ni(II) complexes with a chelating NO -ligand (Carvell et al.). (E) Grubbs catalyst based on a salicylaldiminato ligand.

or co-catalysts such as bis(cyclooctadiene)nickel or $\text{Rh}(\text{acac})(\text{ethene})_2$ to scavenge and remove the deficient donor ligands effectively from solution. Another concept was the direct synthesis of “lightly ligated” complexes primarily based on nitrogen donor ligands (for example pyridine). Based on these findings, the production of polyethene with molecular weights ranging from 8×10^3 to $35 \times 10^4 \text{ g mol}^{-1}$ could be achieved. Unfortunately, early transition metal complexes based on the work of Klabunde and Ittel still lack the ability to copolymerize ethene with methyl acrylates or vinyl acetates.

Neutral nickel(II) complexes with a chelating pyridine-carboxylate ligand were shown to be active in both, the oligomerization of ethene and the copolymeriza-

tion of ethene and CO without the use of a co-catalyst (Fig. 2.3, D) [15]. These complexes are accessible by conversion of the sodium or thallium salt of the anionic N π O-ligand with *trans*-aryl bromobis(phosphine)nickel(II) in tetrahydrofuran [16]. A further development of these compounds are the neutral nickel(II) complexes of Grubbs et al. [17, 18] who succeeded in the synthesis of salicylaldimine-to ligand systems that allowed the investigation of steric and electronic effects on the metal center and afforded polyethenes with molecular weights up to $25 \times 10^4 \text{ g mol}^{-1}$ (Fig. 2.3, E). The degree of branching can be reduced to less than 10 branches per 1000 carbon atoms with increasing bulk of the substituents in the ortho-position of the aromatic ligand. This highly steric constraint simultaneously promotes phosphine dissociation and prevents disproportionation of the ligand. Grubbs complexes are single-component catalysts capable of producing turnover frequencies from 0.5×10^6 to 3.0×10^6 of ethene $(\text{mol of Ni} \times \text{h})^{-1}$ at low temperature and pressure. A further enhancement of the catalyst activity was achieved by exchange of triphenylphosphine against a more labile acetonitrile fragment. Performing the polymerization in the presence of polar additives (1500 equivalents) provides a decrease of molecular weight and turnover frequencies of the neutral nickel catalyst in the following order: ethers > ketones > esters > water > alcohols > tertiary amines. Addition of acids led to a deactivation of the complex without any polymer production. Copolymerization of ethene with functionalized norbornene monomers, carbon monoxide and α,ω -olefins is also possible.

Following the pioneering studies of Keim [19] and Fink [20] in the 1970s and 1980s, mainly Brookhart and coworkers have reported on the development of palladium(II) and nickel(II) diimine complexes (Fig. 2.4, F, G) that polymerize ethene to high molecular weight polymers that have a branched microstructure [21].

The steric demand of isopropyl groups in the 2- and 6-positions of the phenyl moieties was suggested to efficiently block the axial positions of such complexes. As a result, the β -H elimination step is not suppressed in principle, but the elimination product cannot be easily replaced by an incoming olefin molecule that has to approach from the axial direction. Instead, the olefinic double bond is rein-

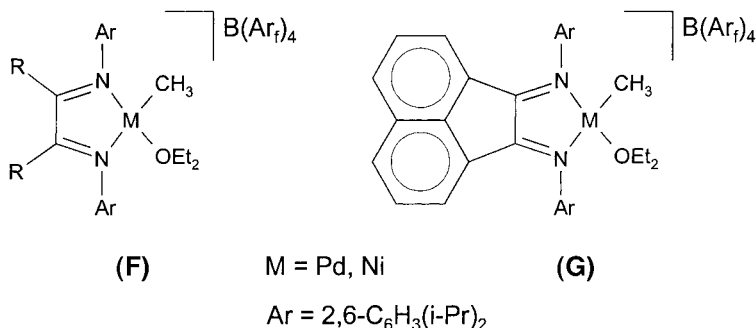


Fig. 2.4 Diimine complexes for ethene polymerization.

serted into the Pd–H species, entailing further chain growth. At the same time, isomerization reactions may take place, which lead to the formation of a unique, highly branched microstructure of the related polymers [9, 22].

2.2

Novel 2,6-Diaryl-Substituted Diimine Catalysts:

A Versatile Concept for Tailored Polymer Properties from Simple C₂ Monomers

The intensive research activities recently focused on late transition metal complexes as polymerization catalysts are justified by decisive improvements in the development of new polymer materials and indicate even more their high potential for future applications. However, up to now they often only dimerize or oligomerize α -olefins due to competing hydride elimination and associative olefin exchange reactions [19]. A new concept of new diimine ligands and complexes bearing 2,6-diphenyl-modified aniline moieties (Fig. 2.5) is still focused on sterically demanding substituents in the 2,6-positions, but it aims further towards the facile modification of the steric and electronic properties of the active species.

A key feature towards potentially stereoselective polymerization reactions involving late transition metal complexes is founded on this novel catalyst generation in which the 2,6-bis(4-*tert*-butylphenyl)aniline building block represents a major perspective. The repulsive steric interactions of the adjacent *tert*-butyl groups were expected to force the diimine ligand to adopt a C₂-symmetric coordination geometry around the metal center. The surrounding chiral complex thereby achieved grants an indispensable prerequisite for achieving stereoselective monomer insertion.

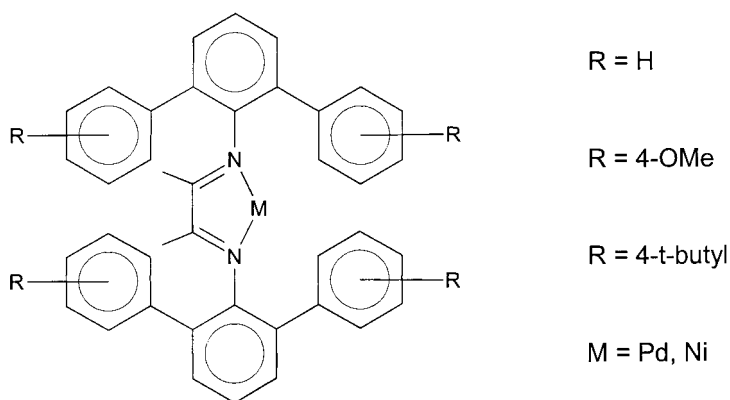


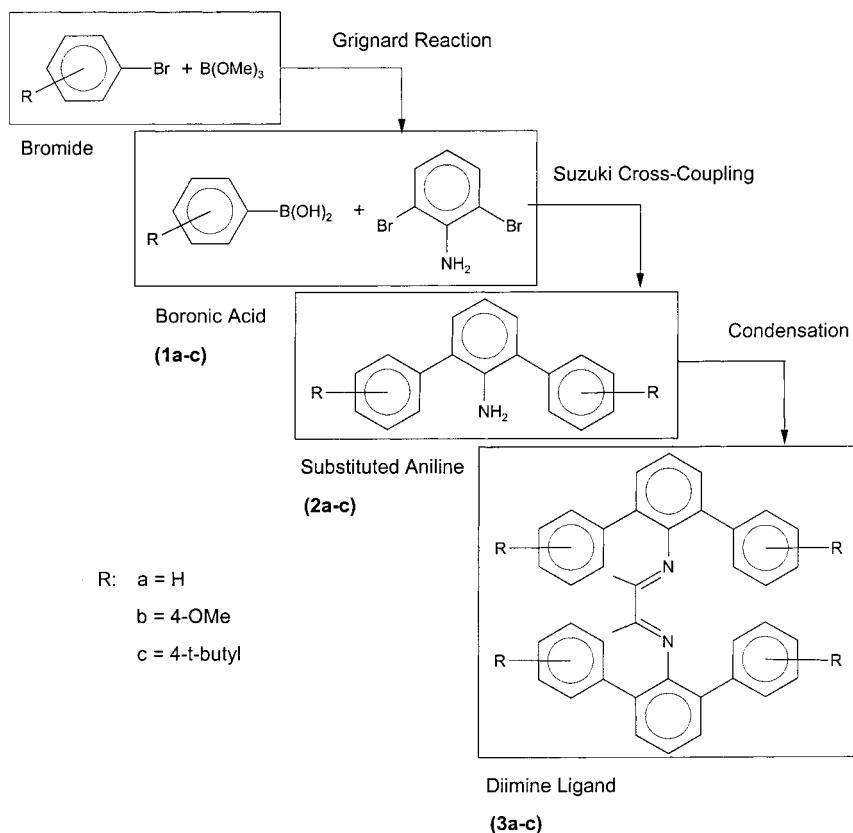
Fig. 2.5 Modified diimine catalysts for ethene homopolymerizations.

2.2.1

Ligand and Complex Synthesis

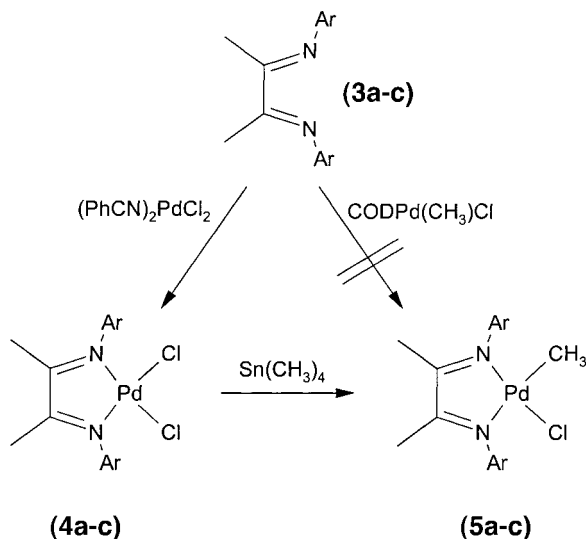
Brookhart's diimine ligands can be obtained by a simple condensation reaction of α,β -diketones with commercially available 2,6-diisopropylaniline [23]. An efficient strategy to access the 2,6-diphenyl-substituted anilines for the present work is the palladium-catalyzed cross-coupling of aryl boronic acids with aryl bromides (Scheme 2.1). Mild reaction conditions, high selectivity, good yields and an adequate tolerance against functional groups make this the method of choice [24]. The aryl boronic acids **1a–c** are easily accessible by simple treatment of the corresponding aryl Grignard compounds with trimethylborate [25].

The Suzuki reactions can be performed via a single-pot protocol by modifying a literature procedure of Miura [26]. The work and time intensive chromatographic workup is substituted by precipitating the amines as hydro chlorides/bromides by addition of the corresponding hydro halogenic acid to the organic layer. After neutralization with aqueous Na_2CO_3 solution, the pure anilines **2a–c** are isolated



Scheme 2.1

Scheme 2.2



from diethyl ether. Subsequently, the terphenyl diimine ligands **3a-c** are prepared by boiling under reflux a solution of 2,3-butanedione and the amino compound in benzene under the catalytic influence of *para*-toluenesulfonic acid. Increasing steric demand of the *para*-substituents requires longer reaction times to isolate the products in good yields (61–85%). Complexes **4a** and **5a** are accessible by reaction of **3a** with CODPdCl_2 at ambient temperature [27]. In contrast, the substituted terphenyl ligands **3b,c** require the use of $(\text{PhCN})_2\text{PdCl}_2$ as precursor complex [28]. Interestingly, the sterically more demanding ligands **3b,c** were highly inefficient in displacing the COD fragment effectively. Treatment of the dichloro complexes (**4a-c**) with $\text{Sn}(\text{CH}_3)_4$ afford the monomethyl compounds (Scheme 2.2, **5b,c**) [29].

2.2.2

Solid State Structures

The structures of the palladium dichloro compounds **4a-c** were determined by single-crystal X-ray analysis. Compounds **4a,c** show disorder which could be resolved satisfactorily. The expected bidentate coordination of the diimine nitrogen atoms to the Pd(II) center, forming square-planar (Fig. 2.6, **4a,b**) and distorted square-planar (Fig. 2.6, **4c**) coordination environments, is found for all three complexes (Tab. 2.1).

The phenyl rings in the 2,6-positions of the aniline moieties point towards each other above and below the N–Pd–N plane as a consequence of the specific location. In **4a**, the terphenyl units are not large enough to feel the steric influence of its symmetry-related counterpart, leading to a complex architecture that is nearly ideal C_{2v} -symmetric. However, already here, the aniline-phenyl rings lack a free rotation around their N–C bond, as confirmed by variable temperature NMR ex-

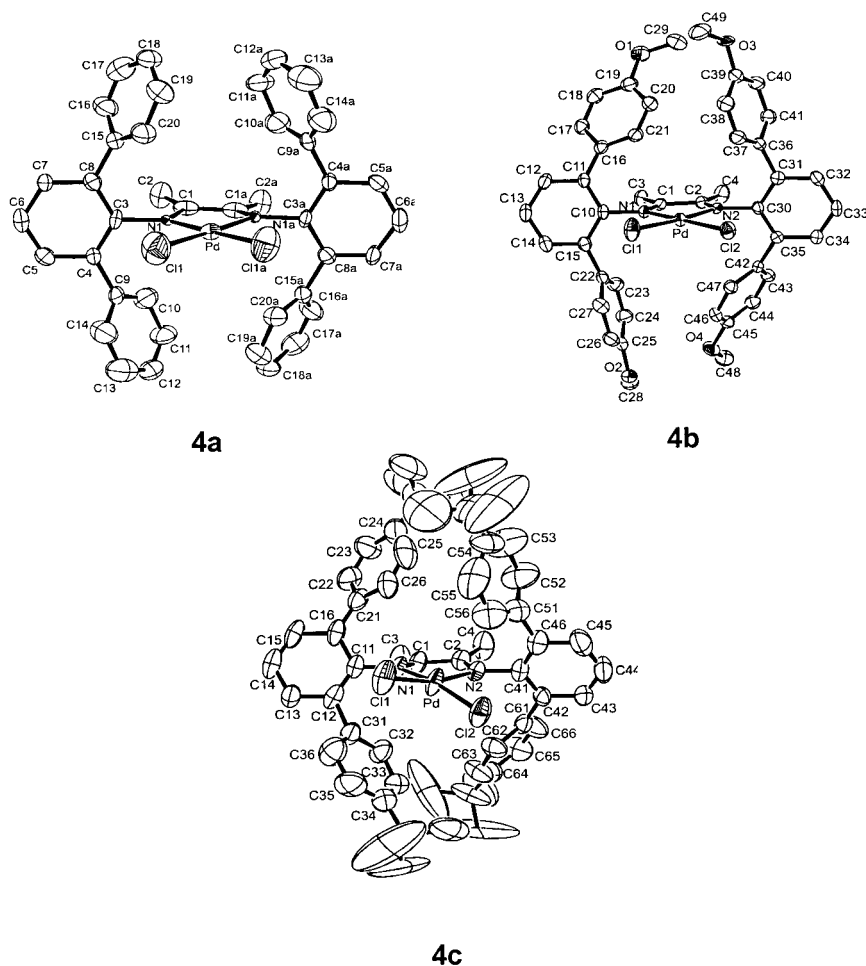


Fig. 2.6 ORTEP plot of complexes **4a–c** showing the atom labeling scheme; atoms labeled “a” were generated by symmetry opera-

tions; thermal ellipsoids are depicted at a 50% probability level. Hydrogen atoms are omitted for clarity.

periments up to 100 °C. Introduction of the 4-methoxy (**4b**, Fig. 2.6) and 4-*tert*-butyl substituents (**4c**, Fig. 2.6) leads to a situation in which repulsive interactions between the fragments pointing towards each other become relevant. This effect is less pronounced in **4b**, because the O–C σ -bond of the methoxy groups provides sufficient possibility of free rotation. This enables the oxygen units to point away from each other which limits extreme structural consequences. In contrast, the *tert*-butyl substituent in **4c** causes a completely different behavior. The racemic complex species adopts a chiral, C_2 -symmetric coordination geometry due to the decisive repulsion of the *tert*-butyl fragments. Definition of the angles ε , ϕ and λ describing the orientation of the phenyl group planes relative to each other

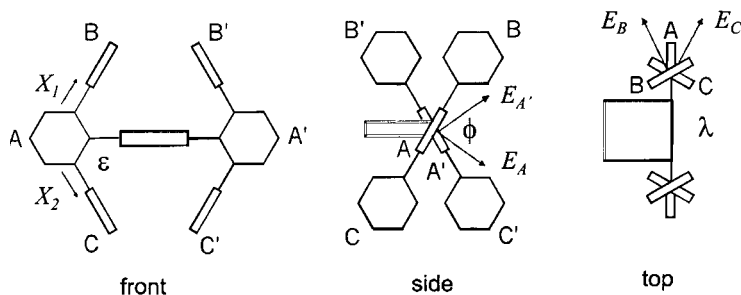
Tab. 2.1 Selected bond lengths and angles for **4a–c**.

<i>4a</i>		<i>4b</i>		<i>4c</i>	
Bond lengths (Å)					
Pd–N1	2.032(7)	Pd–N1	2.034(3)	Pd–N1	2.200(6)
Pd–N1 ^{a)}		Pd–N2	2.022(4)	Pd–N2	2.030(5)
Pd–Cl1	2.205(5)	Pd–Cl1	2.2833(15)	Pd–Cl1	2.271(2)
Pd–Cl1 ^{a)}		Pd–Cl2	2.2984(12)	Pd–Cl2	2.236(2)
N1–C3	1.484(8)	N1–C10	1.460(6)	N1–C11	1.445(9)
		N2–C30	1.457(5)	N2–C41	1.412(9)
C1–C1 ^{a)}	1.482(10)	C1–C2	1.507(6)	C1–C2	1.460(10)
C1–C2	1.532(9)	C1–C3	1.482(6)	C1–C3	1.465(10)
		C2–C4	1.480(7)	C2–C4	1.492(9)
C1–N1	1.300(8)	C1–N1	1.287(6)	C1–N1	1.276(8)
		C2–N2	1.289(6)	C2–N2	1.280(9)
Bond angles (°)					
N1–Pd–N1 ^{a)}	78.9(4)	N1–Pd–N2	78.98(15)	N1–Pd–N2	79.7(2)
N1–Pd–Cl1	98.0(3)	N1–Pd–Cl1	174.23(10)	N1–Pd–Cl1	95.41(17)
N1–Pd–Cl1 ^{a)}	176.9(3)	N1–Pd–Cl2	174.4(8)	N1–Pd–Cl2	164.4(2)
N1a–Pd–Cl1	98.0(3)?	N2–Pd–Cl1	174.23(10)	N2–Pd–Cl1	165.7(2)
		N2–Pd–Cl2	95.9(3)	N2–Pd–Cl2	164.4(2)
Cl1–Pd–Cl1 ^{a)}	85.2(4)	Cl1–Pd–Cl2	89.26(5)	Cl1–Pd–Cl2	92.41(9)

a) Symmetry transformations used to generate equivalent atoms in **4a**: (a) $-x + 2, -y, z$.

(Fig. 2.7) is introduced to give a more quantitative description of the influence of the 2,6-diphenyl substituents.

The planes A, B, and C (A', B', C', respectively) as well as the corresponding plane vectors were calculated by least-squares methods using the relevant X-ray data. The angle ε is defined as that between the vectors \mathbf{X}_1 and \mathbf{X}_2 ; ϕ describes the level of distortion of the “terphenyl wings” and is given as the angle between the plane vectors \mathbf{E}_A and $\mathbf{E}_{A'}$; λ is a measure of the staggered arrangement of the phenyl planes B and C within one “terphenyl wing” and is defined as the angle between the plane vectors \mathbf{E}_B and \mathbf{E}_C . ϕ is 7.5° for the terphenyl complex **4a** indicating the lack of sufficient distortion, as expected. The value of ϕ increases to 27.8° by introduction of the 4-methoxy groups in **4b**, and the structure begins to reduce the steric influence of the para-groups by adopting a distorted conformation in the crystalline state. If the steric demand of the 2,6-diphenyl substituents is enlarged by exchanging the 4-methoxy groups with *tert*-butyl fragments (**4c**), ϕ is increased to 51.4° and the structure finally adopts a distinct chiral, C_2 -symmetric geometry (Fig. 2.6, **4c**; Fig. 2.8). The two substituents pointing to the metal center push the chloride atoms down (or up, respectively), so that the Pd(II) atom is forced to give up its favored square-planar coordination. The steric bulk of the rear pointing 2-(4-*tert*-butyl)phenyl groups also affects the methyl substituents of the backbone, which additionally forces the metallacycle to adopt its chiral conformation.



complex	$\varepsilon[^\circ]$	$\phi[^\circ]$	$\lambda[^\circ]$
4a	127.0	7.5	75.4
4b	125.6	27.8	81.6
4c	138.6	51.4	43.3

Fig. 2.7 Schematic illustration of the most relevant bond angles for **4a–c**.

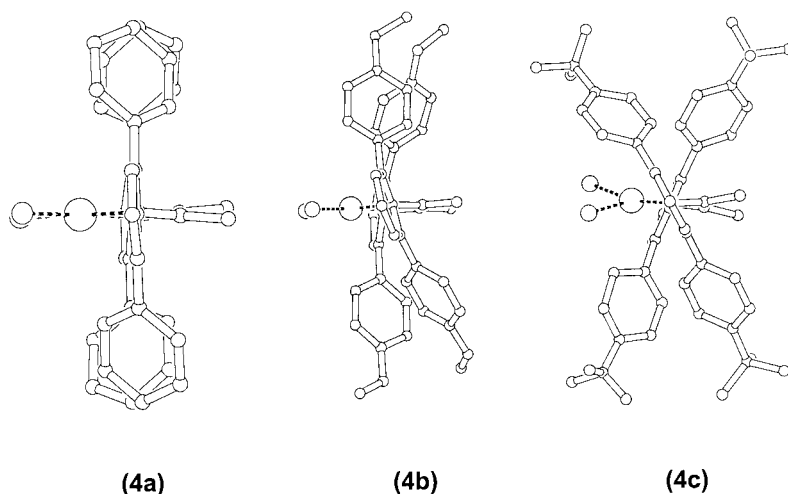


Fig. 2.8 Influence of para substituents on the distortion angle ϕ . A strong increase in ϕ was observed when enhancing the steric demand of the groups at the 4-position.

The cones defined by the ε -angles can be regarded as an indication of the steric shielding of the metal center with respect to the virtual apical positions of the coordination polyhedron. The ε -values are practically identical for **4a,b** (Fig. 2.7: 127.0°, 125.6°, respectively). Interestingly, ε is significantly increased to 138.6° in **4c**. This effect is again attributed to the strong repulsive interaction between the

2-(4-*tert*-butyl)phenyl fragments (Fig. 2.6, **4c**). The planes of the phenyl groups in the 2,6-positions of the aniline moiety form pair-wise chiral elements, which becomes obvious by examination of the top view of the complexes (Fig. 2.7). While there is no significant change of γ for **4a, b** again, this angle decreases to 43.3° in complex **4c** which further supports the stereorigid ligand arrangement, there. However, no signals arising from diastereoisomers can be detected in solution, indicating that rotation is fast, at least on the NMR time scale.

2.2.3

Ethene Polymerization Experiments

2.2.3.1 Palladium Monomethyl Complexes

The polymerization reactions were performed in 50 and 100 mL steel autoclaves in 30 or 50 mL of CH_2Cl_2 at room temperature [30]. Two equivalents of $\text{NaB}(\text{Ar}')_4$ ($\text{Ar}' = 3,5\text{-(CF}_3)_2\text{(C}_6\text{H}_3)$) were added to activate **5a–c**. Remarkably, all three Pd(II) catalysts decompose quickly during the polymerization reaction. This observation can be confirmed by online recording of the monomer consumption. The gas flow declines within the first minutes and is finished after 15–20 min. This fast decomposition is independent of the activation temperature (-78°C or room temperature) and of the presence of monomer. Up to now, no genuine explanation can be given for the unusually high instability of the active species. However, it is evident that the fast decomposition is not the only cause for the low polymer yields; it also prevents the formation of higher molecular weight products (Tab. 2.2).

2.2.3.2 Nickel Dibromides

The corresponding Ni(II) species (**6a–c**) are accessible by *in situ* reaction of (DME)NiBr₂ with the ligands **3a–c** [31]. The activation was performed by treatment of **6a–c** with MAO at ambient temperature in order to avoid decomposition of the active catalyst form as observed for **5a–c**/NaB(Ar')₄. The catalysts **6a–c**/MAO were found to be highly active for ethene homopolymerizations (Tab. 2.3).

Tab. 2.2 Ethene polymerization results with palladium monomethyl complexes.

Run	Catalyst ^{a)}	$p(\text{C}_2)$ [bar]	Yield [g]	M_w [g mol^{-1}]	D	T_m [$^\circ\text{C}$]	N^b
1	5a	30	1.0	11400	1.6	66	58
2	5a	40	0.8	17700	2.3	65	50
3	5b	30	0.7	11600	1.8	78	47
4	5b	40	1.05	10300	1.8	72	50
5	5c	30	0.3	13500	2.0	116	–
6	5c	50	0.3	n.d.	n.d.	116	–

a) **5a, b**: 50, **5c**: 25 μmol .

b) N = branches/1000 C-atoms. Reaction time: runs 1–4: 60 min; runs 5, 6: 10 min.

Tab. 2.3 Ethene polymerizations with nickel catalysts **6a–d**/MAO.^{a)}

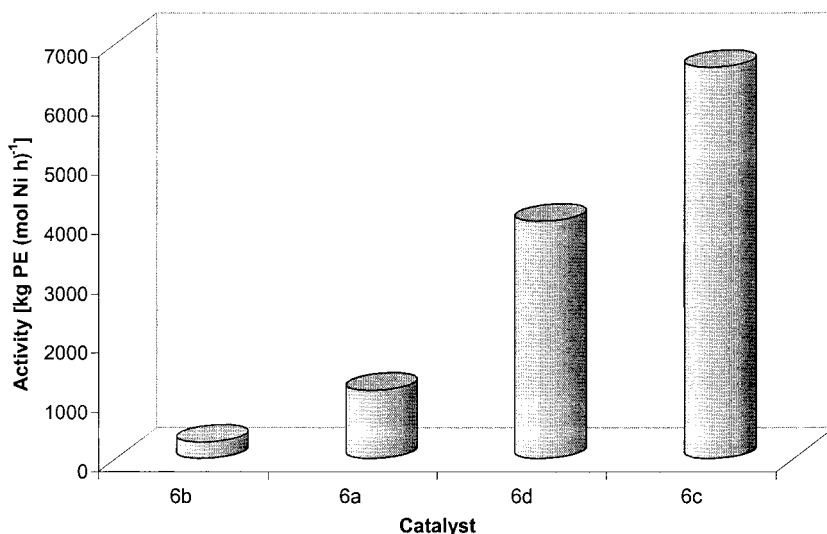
Run	P (C ₂) [bar]	Catalyst	n (Cat.) [mmol]	Time [min]	Yield [g]	Activity [kg (PE) [mol(Ni) h] ⁻¹]	10 ⁻⁶ M _w [g mol ⁻¹]	D	T _m [°C]
1	10	6a	0.04	30	23	1150	n.s.	–	133
2	30	6a	0.04	15	60	6000	n.s.	–	134
3	10	6b	0.04	120	22	275	n.s.	–	132
4	10	6c	0.02	15	33	6600	4.5	1.3	130
5	30	6c	0.02	15	101	20,200	n.s.		130
6	10	6d	0.02	15	20	4000	3.89	2.3	92

a) Experimental conditions: 2 L steel reactor; 800 mL toluene; co-catalyst MAO (Al: Pd ratio 500).

For the 2,6-diphenyl-substituted **6a**/MAO yields are obtained that rival those found for Brookhart's catalyst **6d**/MAO (Tab. 2.3, entries 1 and 6).

At higher monomer concentrations, the activities of **6a–c**/MAO substantially increase and even exceed those of **6d**/MAO under identical conditions. Surprisingly, the chiral complex **6c**/MAO shows by far the highest activities of all investigated catalysts which is pointed out by an increase up to 2×10^4 g(PE) (mol of Ni \times h)⁻¹ at 30 bar ethene pressure (Fig. 2.9). Obviously, the chiral arrangement of the *tert*-butyl-substituted aniline fragments guides the incoming monomer effectively into an optimal coordination position on the Ni(II) center.

2,1-Reinsertions after β -hydride abstraction from the growing chain is effectively suppressed and reduces the probability of the formation of a secondary Ni–C

Fig. 2.9 Comparison of catalyst activities of **6a–d**.

Tab. 2.4 Ethene polymerization reactions with **6c** after hydrogen addition.^{a)}

Run	$c(\text{H}_2)^b)$	Yield [g]	Activity [kg(PE) [mol(Ni) h ⁻¹]	M_w [g mol ⁻¹]	<i>D</i>	T_m [°C]
1	1	45	9000	1,060,000	3.1	135
2	2	45	9000	532,000	2.9	134
3	3	49	9600	449,000	3.0	135
4	6	49	9600	197,000	3.0	136

a) Experimental conditions: 2 L steel reactor; 800 mL toluene; co-catalyst MAO (Al:Ni ratio 500); $n(\text{catalyst})$ 0.02 mmol; $p(\text{C}_2)$: 10 bar. Reaction time 15 min.

b) H₂ addition: pressure burette (10 mL/20 bar portions).

bond (see also the discussion of product linearity below) [32]. This dormant intermediate is known to show significantly lower reaction rates for the next monomer insertion compared to its primary analogues. The low activity of **6b**/MAO (entry 3) clearly results from a reaction with MAO (probably through coordination via the methoxy units) indicated by the formation of an insoluble precipitate directly after MAO addition.

The molecular weight of the polyethenes is beyond the limit of our HT-GPC setup (4.5×10^6 g mol⁻¹) and could thus be determined only in one case (Tab. 2.3, entry 3). DSC measurements clearly indicate a linear character of the ultrahigh molecular weight polyethenes prepared with **6a–c**/MAO (Tab. 2.3, $T_m = 130^\circ\text{C}$). The linearity even surpasses those of the products formed with Brookhart's **6d**/MAO (Tab. 2.3, entry 6) under identical conditions. Quantum mechanical considerations performed on Ni, Pd(II) diimine complexes have provided the first explanation for the high linearity of polyethenes produced with catalysts of high steric demand [33]. Ziegler and co-workers suggested that the formation of branches in the polymer chain originates from rotation of the vinyl chain end which results from β -hydride elimination before a 2,1-reinsertion can occur. The rate of rotation is reduced with increasing steric demand of the ligand system causing higher molecular weights and increased linearity of the polymer products. The same argument was applied to explain the highly linear polyethenes resulting from Fe(II)- and Co(II)-bisimino(pyridine) complexes and might also be accepted as true for complexes such as **6a, c** [34]. The molecular weight of the polymer products can be effectively controlled by addition of hydrogen. The molecular weight could be varied from 2.0×10^5 to 1.0×10^6 g mol⁻¹ dependent on the hydrogen concentrations (Tab. 2.4). The activity significantly increases with addition of H₂ (Fig. 2.10). A reasonable explanation for this effect might be the more homogeneous reaction conditions, but a fast hydrogenation of less reactive intermediates such as those resulting from 2,1-insertions is also conceivable.

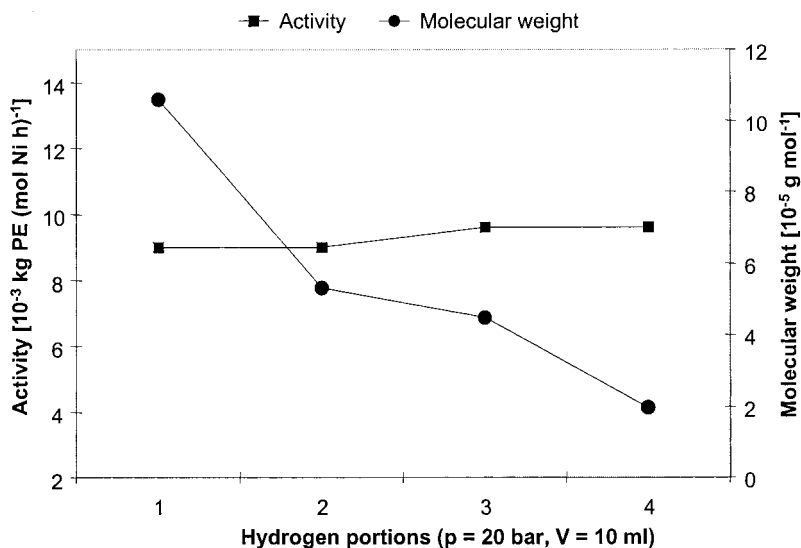


Fig. 2.10 Dependence of molecular weight and activity on the hydrogen concentration.

2.3

Desymmetrized Palladium and Nickel Diimine Catalysts

The new type of palladium(II) and nickel(II) terphenyl diimine complexes based on sterically demanding 2,6-diphenyl-modified aniline moieties provides access to highly active catalysts for the polymerization of ethene [22c, 35]. The steric demand of the *ortho*-aniline phenyl groups was achieved by introducing bulky substituents at the para position leading to generally linear polyethenes. A further advance in modern catalyst design depicts the synthesis of asymmetric diimine ligands bearing the 2,6-diisopropylaniline group on one side and 2,6-diphenyl-modified aniline fragments on the other side of the diacetyl backbone (Fig. 2.11, 8b,c) [36]. Therewith, it is intended to combine the properties of the corresponding symmetric catalysts, allowing one to form primarily linear polyethene bearing a controllable degree of short-chain branches. Such products can be regarded as ethene/propene copolymers (CH_3 -side groups) or as LLDPE-analogues (longer alkyl branches) based on ethene as single component.

2.3.1

Ligand and Complex Synthesis

Diimine ligands can be obtained by a simple condensation reaction of α,β -diketones with suitable aniline derivatives [23]. While the diisopropylamino compound (2e) is commercially available, the terphenyl anilines (2b,c) had to be synthesized via a Suzuki cross-coupling protocol based on 2,6-dibromoaniline and substituted arylboronic acids (1b,c, Scheme 2.1) [26]. Acids 1b,c are easily accessible by treat-

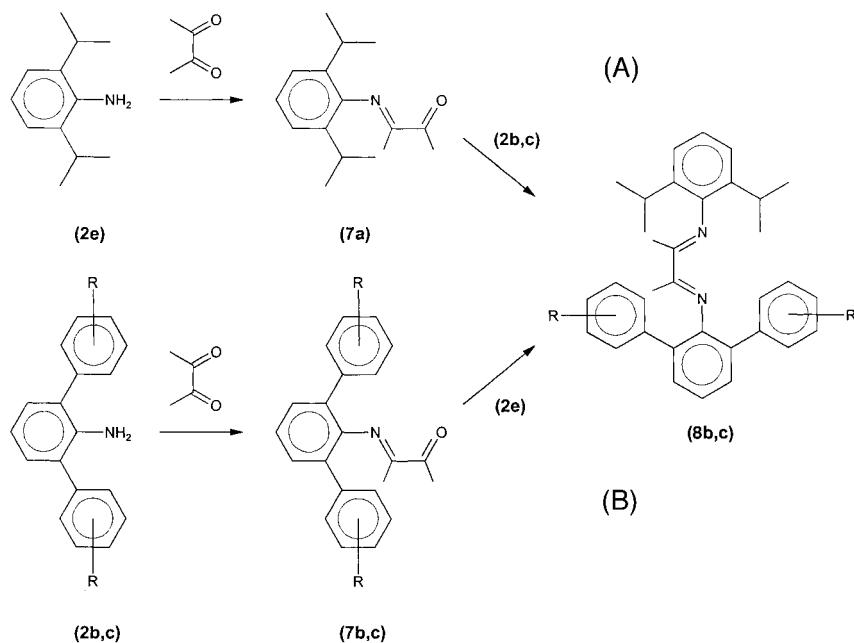


Fig. 2.11 Synthesis of mono condensation products.

ment of the corresponding aryl Grignard compounds with trimethylborate [25]. The huge steric demand of the symmetric diimine ligands requires a synthesis similar to that of the symmetric analogues. The new asymmetric diimine ligands are accessible by a two step procedure. In a first reaction the mono condensation product is synthesized by combination of equimolar amounts of diketone and the corresponding amino compound at ambient temperature. Subsequently, condensation of the resulting ketimine with a further amino component is performed.

Two routes are conceivable for the preparation of the mono condensation product. Route A in Fig. 2.11 starts from the diisopropylaniline (2e) resulting in a liquid ketimine (7a) which can easily be purified by vacuum distillation of the reaction mixture. Route B used the terphenylamino compounds (2b,c) to give the solid products (7b,c). Following these approaches, the *p*-*tert*-butyl substituted (8c) and the *p*-methoxy substituted ligand (8b) can be easily synthesized in yields up to 85%. The corresponding nickel dibromo complexes (Fig. 2.12, 9b,c) resulted from *in situ* reactions of the ligands with (DME)NiBr₂ in toluene solution [37].

2.3.2

Polymerization Reactions

The nickel dibromo complexes were activated for the polymerization of ethene by addition of MAO at ambient temperature. Owing to the high catalyst activities and the precipitating polymers, the polymerization experiments were performed

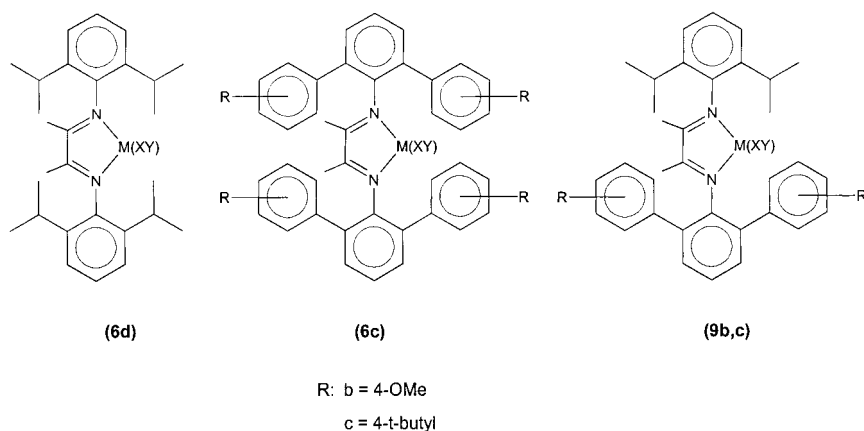


Fig. 2.12 Different architectures of diimine complexes for the polymerization of ethene.

in a 2 L steel autoclave with a strong mechanical stirrer, a prerequisite for achieving controlled conditions during polymerization reaction (Tab. 2.5).

The polyethenes obtained with Brookhart's catalyst (**6d**) had a molecular weight of $4 \times 10^6 \text{ g mol}^{-1}$ and showed a branched microstructure resulting in a broad melting range at around 90°C . NMR measurements indicate about 55 methyl groups per 1000 C-atoms (Fig. 2.13). In contrast, the symmetric terphenyl complex (**6c**) produces high molecular weight, crystalline polyethene which exhibits sharp melting transition at around 130°C . The molecular weights exceed $4.5 \times 10^6 \text{ g mol}^{-1}$ [38].

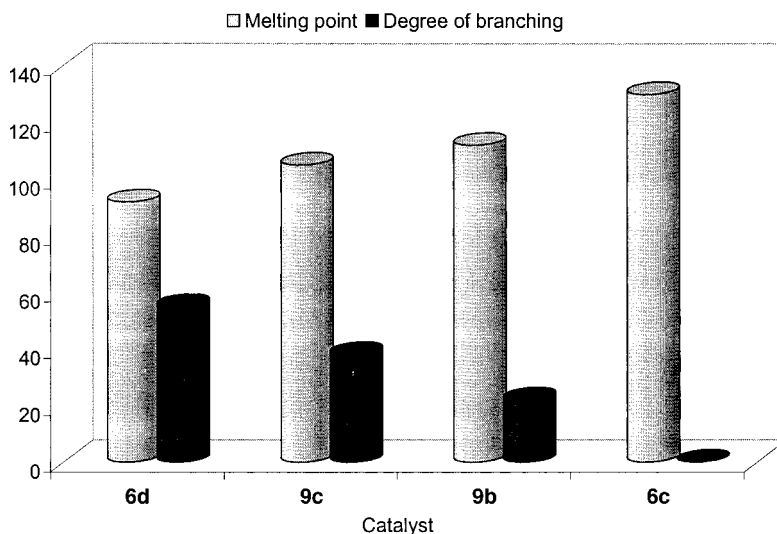


Fig. 2.13 Comparison of melting points and branching degrees for **6c,d** and **9b,c**.

For these products, high temperature NMR experiments gave no indication for methyl branching. The polymers obtained with the asymmetric catalysts (**9b,c**) give melting transitions of 112 (**9b**/MAO) and 105 °C (**9c**/MAO), respectively. The degree of branching is 38 (**9c**) and 22 CH₃ per 1000 C-atoms (**9b**). ¹³C-NMR experiments give decisive evidence that predominantly methyl branches are produced during the polymerization reactions. Only a minor concentration of longer alkyl side chains occur. Complexes **6d,9b,c**/MAO produce ethene/propene copolymers only from ethene as single monomer, while the symmetric substituted complex **6c**/MAO leads to linear high molecular weight homopolymers. Therewith, it is clearly demonstrated that the degree of branching can be controlled by deliberate catalyst design combining aniline moieties with different substituents in the 2,6-positions. This first empirical approach to achieve control of polymer linearity might find a preliminary explanation in an elegant theoretic work of Ziegler et al. [34]. As already discussed above, they assume the degree of branching to be a consequence of the steric hindrance around the active center. Thereby, a precise control of the rate of the associative olefin exchange and of the rate of 2,1-insertion of the vinyl chain end after β -hydride elimination becomes accessible by combination of the isopropyl motif with the more sterically demanding *p*-phenyl substituted anilines. A fine tuning of 2,1- relative to 1,2-insertion seems to take place and enables to control the degree of methyl branching along the linear main chain which leads to ethene/propene copolymers just from ethene monomer.

2.4

Palladium Complexes with Bidentate P \cap N-Ligands: Application in Ethene Oligomerization

Bidentate chelating ligands are often used to fix the active coordination sites of Pd(II) and Ni(II) complexes in a *cis*-arrangement. Besides P \cap O ligands which are industrially used in the SHOP Process, P \cap P and N \cap N ligands are applied in catalytic olefin homo- and copolymerization reactions [21 a, 39]. In our group this concept was successfully extended towards asymmetric late transition complexes by combination of diverse substituted N \cap N ligands. Such catalysts revealed a polymerization behavior that is in between its symmetric analogues and enabled for the first time the synthesis of ethene/propene copolymers only by using ethene as starting compound. Thereby, the influence of the bulky imine substituents plays a decisive role for the polymerization behavior [22 c, 39 a, c]. Molecular modeling results suggest that bulky substituents which occupy the space along the z-axis retard the rate of chain transfer reactions [39 a, c, 40, 41]. We were able to show that the molecular weight of the isolated products is in direct relation to the substitution pattern of the ligand [42]. With respect to the investigations of different N \cap N and N \cap N' ligands we enlarged the field of rational catalyst design by additional studies on bidentate P \cap N complexes. By replacing one nitrogen by an electron donating phosphorus atom we intended a similar and rather more pronounced effect regarding the highly delicate monomer insertion reaction. The required com-

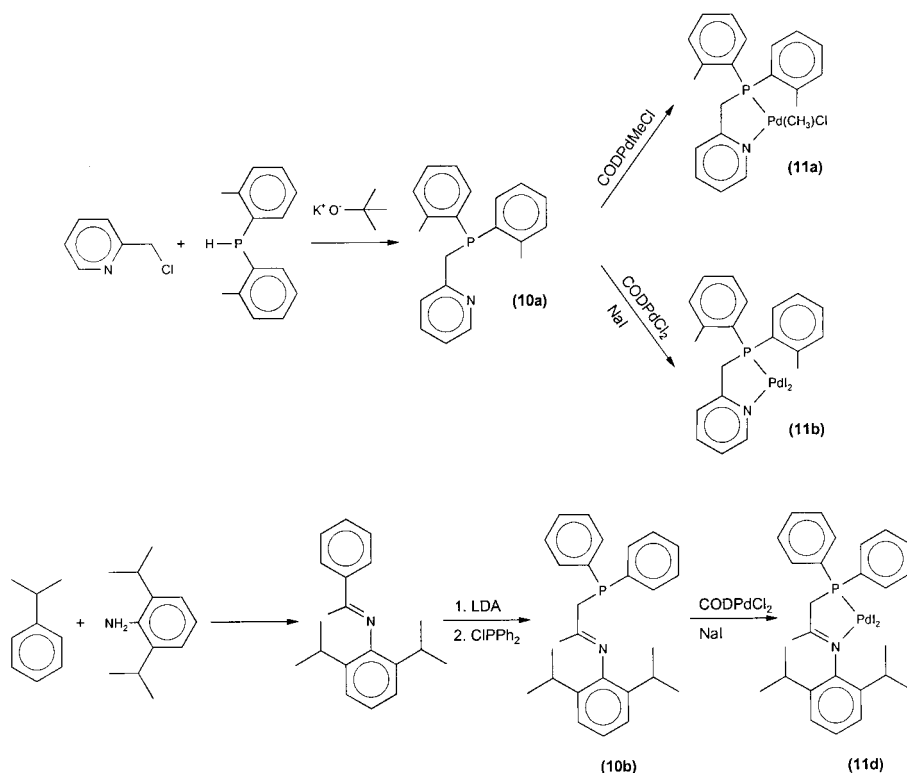


Fig. 2.14 Synthesis of the P∩N ligands **10a,b** as well as of the corresponding palladium complexes **11a–d** (see text for **11c**).

plexes consist of a pyridine and a bis(2-methyl)phenyl substituted phosphane (**10a**) and of an imine and a diphenylphosphane unit (**10b**) [43]. The corresponding palladium complexes are used to examine their catalytic properties (Fig. 2.14).

2.4.1

Synthesis and Characterization

The P∩N ligands **10a,b** as well as the corresponding palladium complexes were synthesized as depicted in Fig. 2.14. Treatment of 2-(chloromethyl)pyridine with one equivalent of bis(2-methylphenyl)phosphane in the presence of potassium *tert*-butylate yielded ligand **10a** which was directly converted into the palladium diiodide complex **11b**. Purification of **11b** was achieved by column chromatography on silica.

The free ligand **10a** was regenerated by treating **11b** with an excess of potassium cyanide. Reaction of **10a** with CODPdClMe afforded the chloromethyl palladium complex **11a**. In square planar P∩N chloromethyl palladium complexes two

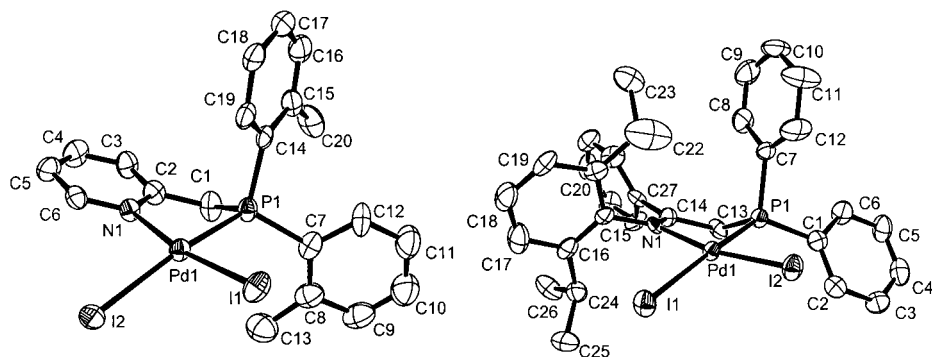


Fig. 2.15 ORTEP plot of the molecular structure of **11b** (left) and **11d** (right).

isomers can be formed (Me *cis* or *trans* to P). In the case of **11a** the formation of a single isomer was observed [44]. It is known that in such square planar complexes ligands with strong *trans* influences prefer a *cis*-arrangement [45]. We assume therefore that **11a** is the isomer in which the methyl and the phosphane groups are oriented in *cis*-position. Such arrangements were also found for other P \cap NPdClMe complexes [46]. The bisacetonitrile complex **11c** was synthesized by treating **11b** with two equivalents of silver tetrafluoroborate in acetonitrile. Complexes **11a–c**, which are stable in solution, were characterized by FAB-MS, elemental analysis, IR as well as ^1H - and ^{31}P -NMR analysis. The condensation of acetophenone and 2,6-diisopropylaniline afforded the imine which was deprotonated with lithium diisopropylamide (LDA). Subsequent addition of chlorodiphenylphosphane yielded ligand **10b** in about 65% yield. The ligand was converted directly into the palladium diiodide complex **11d** which was purified by column chromatography. However, complex **11d** proved to be unstable in solutions (halogenated solvents) as could be seen by the increase of several new signals in the ^{31}P -NMR with time. Attempts to prepare the chloromethylpalladium complex of **10b**, either by the treatment of **11d** with SnMe_4 or by regeneration of the free ligand **10b** with KCN and subsequent reaction with CODPdClMe were unsuccessful.

Single crystals of **11b,d**, suitable for an X-ray structure determination could be obtained by crystallization from $\text{EtAc}/\text{CH}_2\text{Cl}_2$. An ORTEP plot of both structures is depicted in Fig. 2.15. Characteristic bond lengths and angles are listed in Tab. 2.6. The P \cap N ligands and the iodine atoms together form a distorted, square planar coordination sphere around the metal center (**11b,d**).

In both complexes, **11b,d**, the Pd–I bond *trans* to the phosphorus atom (Pd1–I2 in **11b** and Pd1–I1 in **11d**) is longer (0.08 and 0.09 Å) than the Pd–I bond *trans* to the nitrogen atom, which might be attributed to the larger *trans* influence of the phosphorus compared to nitrogen (imine and pyridine) [45]. In the solid state one of the *o*-aryl substituents in complex **11b,d** (methyl in the case of **11b** and isopropyl in the case of **11d**) is oriented above/below the coordination plane. A connection between shielding of the metal center along the *z*-axis and chain transfer reactions was found for several diimine complexes [22c, 33b, 41, 42c].

Tab. 2.5 Polymerization experiments with nickel dibromo complexes.

Run	Catalyst	n (Cat.) [μ mol]	Time [min]	Activity [kg(PE) [mol(Ni) h ⁻¹]]	$10^6 M_w^a$ [g mol ⁻¹]	D	N^b	T_m^c [°C]
1	6d	20	15	4000	3.98	2.3	55	92
2	9b	40	60	1200	>4.0	–	22	112
3	9c	40	60	400	>4.0	–	38	105
4	6c	20	15	6500	>4.0	–	0	130

p (Ethene): 10 bar.

a) Measured in 1,2,4-trichlorobenzene at 135 °C; all molecular weights relative to narrow polystyrene standards; molecular weights of more than 4.0×10^6 are outside of the range of the used GPC set-up.

b) Methyl groups/1000 carbon atoms (predominantly methyl branches).

c) Determined by DSC measurements.

2.4.2

Ethene Oligomerization Reactions

Different P \cap N ligands were applied in olefin polymerization as well as in olefin/CO copolymerization [9, 43, 47]. Complex **11a** was tested for ethene polymerization in CH₂Cl₂ after activation of the complex with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF) in diethyl ether. The reaction products were characterized by GC/MS which was calibrated using commercially available α -olefins (1-octene, 1-decene and 1-dodecene) as standards. Oligomers with molecular weights between 112 g mol⁻¹ (C₈) and 448 g mol⁻¹ (C₃₂) were detected. As expected, only signals for olefins with an even number of carbon atoms were observed. In the GC/MS spectra for each C_n-fraction (C₈–C₃₂) one intense as well as several less intense signals were detected. We attribute the main signal to the linear α -olefin (in accordance with our linear standards used for calibration). An influence of the polymerization pressure on the isomer distribution could not be determined as was also found for other palladium catalysts [39a]. At 10 and 60 bar the content of 1-octene within the C₈-fraction was 94 and 98%. Comparison of the results of runs 1 and 2 suggests that at higher ethene pressure the formation of higher molecular weight oligomers is favored, as expected. The catalyst system **11a**/NaBAF, as well as the corresponding palladium systems containing the P \cap P ligand 1,3-bis((bis(2-methylphenyl)phosphino)propane ((2-Me)₂P \cap P(2-Me)₂)) or the (py)N \cap N(im) ligand (pyridine and 2,6-diisopropylphenyl substituted imine) oligomerize ethene to an isomeric mixture of olefins [39d, 42a]. The contents of the linear olefins is significantly higher for the catalyst system **11c**/NaBAF (94%) than for the system containing the (2-Me)₂P \cap P(2-Me)₂ ligand (α -olefins <5%). Besides, the maximum chain length obtained with **11c** (C₃₂) is significantly higher than with the (2-Me)₂P \cap P(2-Me)₂ (C₁₆) system. In polymerization experiments with (py)N \cap N(im) several isomers of the C_n fraction were obtained (for example

nine isomers of the C₁₀-fraction) [48]. Catalyst system **11a**/NaBAF was tested for ethene/CO copolymerization reactions. However only traces of α -olefins could be isolated, which were probably formed during the initiation of the reaction, before CO was added to the pressure autoclave. The bisacetonitrile complex **11c** showed no activity for the copolymerization of ethene and CO at room temperature (using methanol as co-catalyst).

2.5

Application of Sterically Demanding Bis(phosphino) Complexes in Ethene Homopolymerization

Brookhart's report on the synthesis of high molecular weight polyolefins concentrates mainly on Ni(II) and Pd(II) catalysts bearing isopropylidimine ligands [21a, 22a, 49]. His concept was developed further and rather surpassed by enlarging the steric bulk, leading to increased molecular weights, higher polymerization activities and, what is most interesting, to highly linear polyethene products. In addition, focus on desymmetrized complexes bearing two different diimine ligands revealed polyethene materials with predominantly methyl branches. The steric demand of the bulky isopropyl substituents on the aniline moieties and their orientation towards the virtual apical positions of the square-planar complexes were found to be crucial for an optimal alignment of the incoming monomer relative to the growing polymer chain. Obviously, increased screening of the metal center blocks associative olefin exchange, retards chain transfer and adjusts the degree of branching [22]. Up to now, phosphine complexes have been known (with few exceptions) to produce only oligomeric products, which has been utilized to manufacture higher α -olefins in several technical processes [10, 14, 19a,b, 50]. Hence, it is of considerable interest as to whether the concept outlined above is transferable from N \cap N (N \cap N', respectively) over P \cap N to bis(phosphine)-based complexes. The more so if one takes into account that phosphine catalysts display a significantly improved stability towards polar monomers (for instance CO) and higher monomer concentrations [51]. To answer this question and to evidence the assumption that the steric environment is the decisive factor towards high molecular weight polymers, a model study was conducted in which the 1,2-bis(diphenylphosphino)ethane (DPPE) served as basis for the design of new, sterically demanding bis(phosphine) ligands for the polymerization of olefins.

2.5.1

Synthesis and Complexation of Ethene Bridged Bis(phosphine) Ligands

Ethene bridged bis(phosphine)s are most conveniently prepared by the reaction of 1,2-bis(dichlorophosphino)ethane with organometallic reagents, usually lithiated or Grignard compounds [52]. This method prevents the time consuming and laborious synthesis of secondary phosphines and easily affords the desired bidentate phosphines via a single-pot procedure. Accordingly, the bromobenzene derivatives

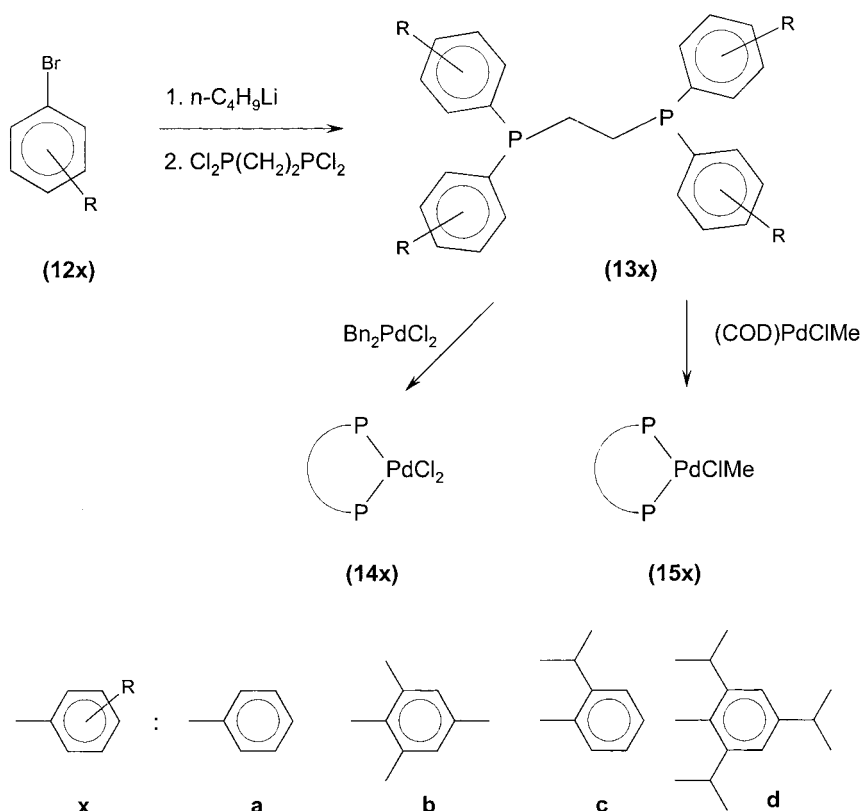


Fig. 2.16 Synthesis and complexation of the bis(phosphine)s **13x**.

12b–d were treated with an equimolar amount of *n*-butyllithium at -70°C in dry tetrahydrofuran. Subsequently, 1,2-bis(dichlorophosphino)ethane was introduced. After work-up, pure 1,2-bis(di(2,4,6-trimethylphenyl)phosphino)ethane (**13b**), 1,2-bis(di(2-isopropylphenyl)phosphino)ethane (**13c**) and 1,2-bis(di(2,4,6-triisopropylphenyl)phosphino)ethane (**13d**) were obtained in moderate to high yields after recrystallization of the crude product (Fig. 2.16). Yields of more than 90% for **13b** compared to 19% obtained using the method of Chatt et al. [53] clearly underline the big advantage of this straightforward procedure.

The reaction of **13x** with bis(benzonitrile)dichloropalladium(II) [Bn_2PdCl_2] and monochloro(1,5-cyclooctadiene)monomethylpalladium(II) [(COD) PdClMe] yielded the corresponding palladium(II) complexes **14x** and **15x** (Fig. 2.16). Upon slow evaporation of an acetonitrile solution, **14c** and **14d** gave crystals that were suitable for structure determination via single crystal X-ray diffraction (Fig. 2.17). Compound **14b** was crystallized by slow diffusion of pentane into a solution of **14b** in tetrachloroethane.

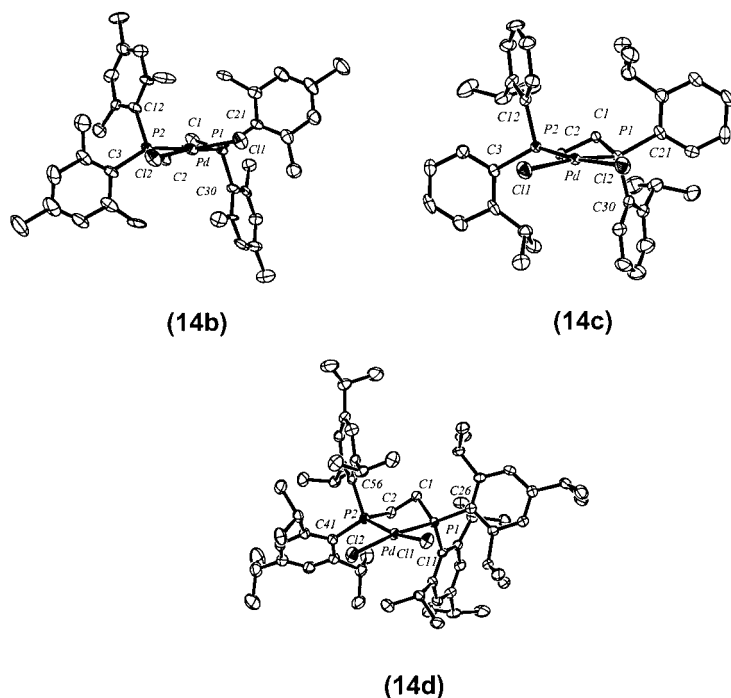


Fig. 2.17 Crystal structure of compound **14b–d** (ORTEP-plot, thermal ellipsoids depicted with 50% probability). Solvent is omitted.

2.5.2

Solid State Structures

The palladium(II) complex **14b** crystallizes in the monoclinic space group $P2_1/c$ (Fig. 2.17, Tab. 2.7).

Four molecules of tetrachloroethane were found in the unit cell per one metal atom. Two of them are highly distorted and poorly defined which gets clear and distinct in the high R -value obtained for **14b**. The complex molecule itself, however, is reasonably well refined. Attempts to use partial occupation factors for solvent molecules were not successful. Compound **14c** formed monoclinic crystals which belong to the space group $P2_1/n$ and complex **14d** (Fig. 2.17, Tabs. 2.8, 2.9) gave triclinic crystals of space group $P1$ ([DPPE] $PdCl_2$): $P2_1/c$ [54]).

Two molecules of acetonitrile were found to be enclosed within the unit cell of **14d**, whereas **14c** contains one acetonitrile per unit cell. An increased $P1-Pd-P2$ angle of $88.54(4)^\circ$ in **14d** compared to $86.98(7)^\circ$ in **14c** or $85.82(7)^\circ$ in DPPE- $PdCl_2$ **14a** (solvated with one molecule of dichloromethane) was observed, which reflects the steric demand of the isopropyl moieties. [DPPE] $PdCl_2$ shows approximately a square-planar arrangement of the two P and two Cl atoms around the Pd center. In contrast, in **14b–d** the square-planar coordination is highly distorted.

Tab. 2.6 Selected bond lengths and angles of complex **11b**, d.

<i>Bond length [Å]</i>			<i>Bond angles [°]</i>
11b			
I1–Pd1	2.5731(11)	N1–Pd1–P1	83.17(15)
I2–Pd1	2.6608(8)	P1–Pd1–I1	90.22(5)
Pd1–N1	2.100(5)	N1–Pd1–I2	94.63(14)
Pd1–P1	2.2298(18)	I1–Pd1–I2	93.11(3)
11d			
I1–Pd1	2.6531(13)	N1–Pd1–P1	81.9(3)
I2–Pd1	2.5744(12)	P1–Pd1–I2	92.18(8)
Pd1–N1	2.131(9)	N1–Pd1–I1	94.7(2)
Pd1–P1	2.223(3)	I2–Pd1–I1	92.14(4)

Tab. 2.7 Selected bond lengths and bond angles for **14b**.

14b · 4(CCl₂H)₂			
<i>Bond lengths [Å]</i>		<i>Bond angles [°]</i>	
Pd–P1	2.255(2)	P2–Pd–P1	87.95(8)
Pd–P1	2.268(2)	Cl2–Pd–Cl1	94.68(8)
Pd–Cl1	2.382(2)		
Pd–Cl2	2.374(2)	C30–P1–C21	106.8(4)
		C30–P1–C1	100.5(4)
P1–C21	1.861(9)	C21–P1–C1	113.0(4)
P1–C30	1.834(9)		
P1–C1	1.867(9)	C2–P2–C3	111.0(4)
		C2–P2–C12	99.0(4)
P2–C3	1.840(9)	C3–P2–C12	107.6(4)
P2–C2	1.833(9)		
P2–C12	1.843(9)		

We have further compared **14c,d** and [(DPPE)PdCl₂] after calculating the mean planes of PdCl₂P₂ sequence [55]. At least in the solid state the coordinated atoms of [(DPPE)PdCl₂] show minimum deviations from the 5-atom plane (about 0.04 Å) and the shortest Pd–P bond lengths (2.233(2) and 2.227(2) Å) of all complexes. The 2-isopropyl substituted compound **14c** exhibits moderate deviations from planarity (about 0.13–0.14 Å) and longer Pd–P bond lengths (2.256(2) and 2.252(2) Å). 2,4,6-Isopropyl substituted **14d** reveals the largest deviation from the mean plane (approximately 0.20 Å) and the longest Pd–P bonds in general (2.278(10) and 2.3041(11) Å). In **14b** the deviations of the PdCl₂P₂ unit from the square planar coordination plane, the P1–Pd–P2 angle and the Pd–P bond lengths are between those found for **14c** and **14d**. In each compound the Pd atom itself is approximately in the five atom mean plane. The distortion of coordinated

Tab. 2.8 Selected bond lengths and bond angles for **14c**.

14c · 2CH₃CN			
Bond lengths [Å]		Bond angles [°]	
Pd–P1	2.256(2)	P1–Pd–P2	86.98(7)
Pd–P1	2.252(2)	Cl1–Pd–Cl2	94.32(7)
Pd–Cl1	2.357(2)		
Pd–Cl2	2.348(2)	C21–P1–C30	106.8(3)
		C21–P1–C1	107.2(3)
P1–C21	1.817(7)	C30–P1–C1	106.4(3)
P1–C30	1.826(7)		
P1–C1	1.839(7)	C3–P2–C2	108.2(3)
		C3–P2–C12	106.8(3)
P2–C3	1.822(7)	C2–P2–C12	106.6(3)
P2–C2	1.833(7)		
P2–C12	1.833(7)		

Tab. 2.9 Selected bond lengths and bond angles for **14d**.

14d · CH₃CN			
Bond lengths [Å]		Bond angles [°]	
Pd–P1	2.2780(10)	P1–Pd–P2	88.85(4)
Pd–P1	2.3041(11)	Cl1–Pd–Cl2	91.55(4)
Pd–Cl1	2.3462(11)		
Pd–Cl2	2.3513(11)	C1–P1–C11	100.34(16)
		C1–P1–C26	112.15(15)
P1–C26	1.862(3)	C11–P1–C26	104.56(14)
P1–C11	1.852(3)		
P1–C1	1.843(3)	C2–P2–C41	111.54(16)
		C2–P2–C56	96.03(15)
P2–C56	1.872(3)	C41–P2–C56	105.02(15)
P2–C41	1.856(4)		
P2–C2	1.848(3)		

atoms tends towards a tetrahedral environment. The Pd–Cl bond lengths are surprisingly constant. They vary between 2.3462(11) Å for **14d** and 2.357(2) Å and consists of slightly longer values for **14b,c**. As a first conclusion one can say that the amount of substitutions of the phenyl rings is significantly correlated to the increasing Pd–P bond lengths, widening of the P1–Pd–P2 bond angle and to high distortion from the square-planar coordination geometry [56]. Furthermore, the crystal structures of **14c,d** indicate that in both complexes isopropyl substituents are located in axial positions above and below the coordination plane. This charac-

teristic is also found for the solid state structure of Brookhart-type diimine catalysts that produce high molecular weight polyolefins [9].

2.5.3

NMR Studies on the Palladium Dichloro Species

By formation of the complex **14c**, the pattern of resonances of the bis(phosphine) **13c** (^1H - and ^{13}C -NMR) significantly changed in such way that additional signals appeared in the aromatic as well as in the aliphatic region. The ^1H -absorptions of **14c** are broad and do not display a clear splitting of the NMR signals. The 500 MHz ^1H -NMR spectrum revealed eight resonances which belong to aromatic hydrogens (two of them are superimposed). These observations suggest that two different orientations of the aromatic groups are realized in solution which interconvert on the NMR time scale [57]. This is confirmed by ^1H , ^1H -COSY experiments. The signals are divided into two sets, each resembling one of the suggested arrangements. Accordingly, the methylene (bridge) and the methine (isopropyl) resonances are split into two signals. If the ^1H -NMR spectra are recorded at elevated temperatures (up to 90°C), the absorbences will gradually change their line shape and position. At 90°C , molecular motion seems to proceed almost unrestrictedly. NMR spectra of complex **14b,d**, however, exhibit well-defined ^1H -absorptions with a clear splitting pattern. In case of **14d** the absence of fluxional phenomena is caused by additional isopropyl units in the 6-positions of the aromatic rings. This prevents the type of molecular motion that is still found for **14c**. As a consequence, the theoretical number of resonances in **14d** is doubled compared to the ligand **13d**, although some of them are superimposed, too. In contrast, the methyl substituents in **14b** are not bulky enough to provide any visible effect on the molecular flexibility of the complex. The number of resonances of **14b** is equal compared to the free ligand (**13b**). The solid state structures support these interpretations.

2.5.4

Influence of Substitution on Ethene Polymerization Reactions

In order to investigate the influence of the substitution pattern on the polymerization behavior, compounds **15a–d** were treated with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [$\text{NaB}(\text{Ar}_f)_4$, $\text{Ar}_f = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$]. After chlorine abstraction the generated monocationic species were tested in ethene polymerization experiments [9]. The large anion $\text{B}(\text{Ar}_f)_4$ is known to have a reduced tendency to coordinate to the electrophilic palladium(II) center. Thereby, small amounts of acetonitrile, which can be easily replaced by incoming monomers, are added to stabilize the monocationic species through coordination on the free sites. The quantitative formation of the monocationic species was proved by ^{31}P -NMR spectroscopy [58]. The solution of the catalytically active species was diluted with 20 mL dichloromethane and transferred into a 100 mL stainless steel autoclave equipped with a magnetic stirring bar and a glass inlet. The autoclave was pres-

surized with 60 bar of ethene. Subsequently, the mixture was stirred for 24 h at ambient temperature. Besides the C_4 -product formed by the dimerization of ethene, compound **15a** with 1,2-bis(diphenylphosphino)ethane (DPPE) as phosphine ligand produced hexene isomers that could be detected by GC/MS measurements (Fig. 2.18).

An increase of the steric environment to 2,4,6-trimethyl (**15b**) generated higher olefins in addition to the ones just described. These were identified as oligomeric units up to C_{20} . A further change of the substitution to an isopropyl group in 2-position of the phenyl unit (**15c**) revealed only a small influence on the product distribution. Interestingly, **15b,c** favored the formation of a single isomer in every fraction. Comparison with reference olefins confirmed that this compound is the linear terminal olefin. The selectivity towards linear products is more pronounced for **15c**. Here for instance, the C_8 -fraction contained about 52% 1-octene, the rest consisted of a mixture of internal or branched olefins whose chemical composition was not investigated. In case of ligand **15d** variable amounts of a white solid

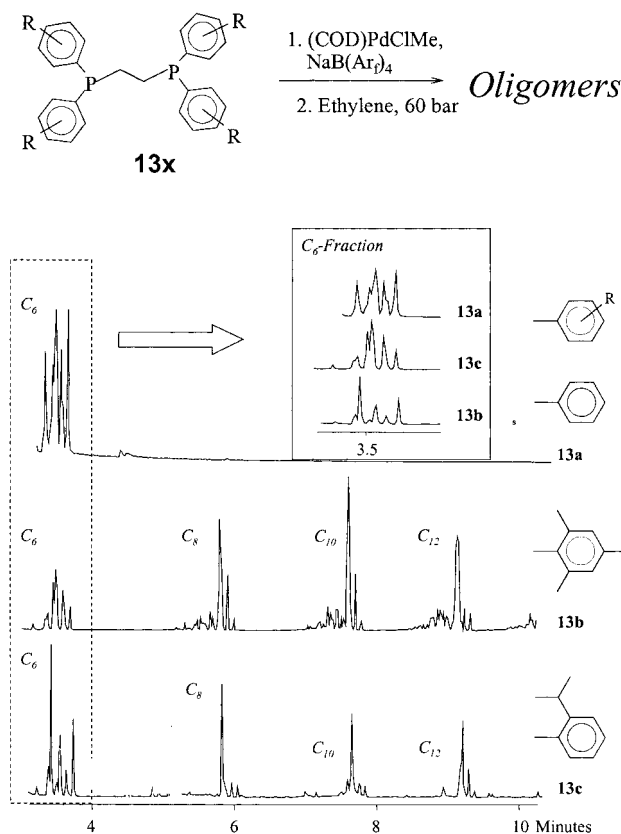


Fig. 2.18 GC chromatograms of the ethene oligomers, resulting from complexes **15x**

could be isolated. Oligomeric products were not detected by GC. DSC measurements showed a melting point of 137.0 °C ($\Delta H_f = 213.52 \text{ J g}^{-1}$) for the material (heating rate 10 K min⁻¹). In the IR spectrum bands at 2919 and 2849 cm⁻¹ (C–H-stretching, CH₂), 1469 cm⁻¹ (C–H-deformation, CH₂) und 718 cm⁻¹ (CH₂-rocking) were observed. ¹H-NMR measurements in *para*-xylene-d₁₀ at 90 °C provided a main resonance at 1.52 ppm (CH₂, main chain) and a weak signal at 1.09 ppm (CH₃, side chain). The ¹³C-NMR spectrum revealed only one resonance at 29.97 ppm (CH₂, main chain). GPC measurements in 1,2,4-trichlorobenzene at 145 °C gave a molecular weight M_w of $1 \times 10^5 \text{ g mol}^{-1}$ and a polydispersity of 3.6. On the basis of the analytical results, the white solid material was identified as a predominantly linear, semi crystalline polyethene with a relatively high molecular weight belonging to the class of High Density Polyethenes (HDPEs) [59].

The polymerization results clearly demonstrate that also in the case of bis(phosphine)s the steric demand of the ligand sphere is a prerequisite for the formation of higher olefins from ethene (**15b,c**). At the same time, there occurs a moderate, but observable selectivity for linear products. It was revealed that only the highly sterically crowded 2,4,6-triisopropylphenyl substitution efficiently acts in blocking the axial positions of the tested compounds. Here, the associative displacement of β -H elimination products by free monomer is retarded in a way that allows the formation of polyethenes with high molecular weights. The polymerization behavior of **15b–d** reflects the observations in NMR spectroscopy concerning the conformational rigidity of the ligand spheres. Only the highly rigid ligand architecture of **14d** efficiently fixes the substituents (isopropyl units) above and below the coordination plane and enables the complex to work as a polymerization catalyst. The predominantly linear character of the polymers produced using **15d** disagrees with reports on highly branched amorphous polyethenes formed by diimine-Pd systems. An explanation for this difference may again be derived from quantum mechanical considerations performed on Ni(II), Pd(II)-diimine complexes [33]. There it is suggested that an isomerization of the polymer chain attached to the metal center – which can result in the formation of a side group – mechanistically requires a rotation of the polymer chain. The axis for this rotation would be the olefin-to-metal bond of the olefinic end group (vinyl end group) formed by a β -H elimination process. A methyl side group would then be formed by reinsertion of this vinyl end group in a 2,1-fashion, whereby a new monomer unit is incorporated. According to these calculations, such a mechanism will not take place step by step but rather in a simultaneous way. Under these circumstances, an increase in the steric demand of the ligand sphere may suppress chain rotation which is necessary in obtaining branched polymer microstructures. This will – if the reinsertion of the vinyl end group alternatively takes place in a 1,2-orientation – finally lead to the formation of less branched, more linear polymers. This argument was used to explain the linearity of the polyethenes resulting from Fe(II)- and Co(II)-bisimino(pyridine) complexes and might also be accepted as true for bis(phosphine) catalysts such as **15b–d** [34].

2.6

Conclusion

In recent years late transition metals have rapidly established an excellent reputation in the field of catalytic α -olefin polymerization. Progress in catalyst architecture of late transition metal compounds have indicated their great ability as industrially relevant polymerization catalysts. Further decisive discoveries are expected to grow more rapidly than in any other homogeneous catalyst family. Despite their prosperous potential, late transition metal catalysts still lack the possibility to provide reliable control of polymer microstructure and to access high molecular weight polymers. Therein, these compounds still have to contend with the dominance of early transition metallocene complexes. Starting with the development of the first diimine complexes at least a strong increase of the molecular weight could be achieved. Deliberate structural variations now enforce further improvements and open the door to new polyethylene materials. Intrinsically incidental isomerization reactions enable a precise control of the polymer microstructure and are – in contrast to early transition metal compounds – not detrimental to the catalyst performance. By variation of the steric environment, polyethenes from highly linear to highly branched are adjustable. The rich portfolio of synthetic methods applicable in nitrogen and phosphorous chemistry establishes a new type of (late transition metal) olefin polymerization catalysts that possibly point to several future fields of interest: (1) microstructural control via improved catalyst architectures; (2) copolymerization of apolar olefins with functional monomers; (3) increase of polymerization activity; (4) identification of polymerization-active species. In contrast to most of the known catalyst systems, for which structure variations are limited or even not possible, the presented complexes have a variable structure possessing high potential for the design of new polymer materials. In case of the bulky 2,6-di(4-*tert*-butylphenyl)aniline substituted complex **4c** a chiral, stereorigid arrangement showing distinct C_2 -symmetry was obtained. The pronounced steric influence of these ligands on the metal center results furthermore in a distortion of the square-planar coordination geometry which is in its extent strongly dependent on the bulkiness of the ligand structures. The C_2 -symmetry resembling the *rac*-form of symmetrically bridge metallocene complexes might provide future control of the stereochemistry in α -olefin homo- and copolymerization reactions. By desymmetrization of Brookhart type diimine complexes, a different but not less important achievement was obtained. Combination of two diverse amine units affords the formation of ethene propene copolymers by ethene as single monomer with simultaneous control of copolymer linearity. Transfer of these facts towards P \cap N ligands only partly succeeded. The existence of a distorted, square planar coordination sphere for the palladium diiodide complexes resembles the previous results of symmetric and asymmetric N \cap N complexes. However, only oligomerization of ethene occurred after activation with a borate salt, which is may be attributed to the insufficient steric demand of the investigated compounds. These systems produce a mixture of olefins with a high content of the linear α -olefin. Sufficiently high steric demand as the key to polymeric olefin

products also plays a decisive role for bis(phosphine) complexes. A consecutive increase of the steric demand from 1,2-bis(diphenylphosphino)ethane (DPPE) is associated with a change from oligo- to polyolefins as reaction product in ethene polymerizations [60].

2.7

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3

Highly Active Ethene Polymerization Catalysts with Unusual Imine Ligands

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3.1

Introduction

The commercial production of polyolefins from ethene and propene was greatly progressed with the discovery of what came to be known as Ziegler–Natta catalysts and Phillips & Union Carbide type catalysts [1]. They opened the possibility of preparing polyolefins with new and interesting material properties under what at that time would be considered mild conditions with respect to pressure and temperature. A further impact in this area came from the observation that mixtures of alkylating agents with metallocene halides of Groups 3 and 4 catalyze 1-olefin polymerization [2]. These “single site” catalysts differ from their heterogeneous counterparts in that they are (in theory) truly single sited, i.e. only one type of a coordinatively unsaturated complex is involved in the migratory insertion of the olefinic monomer. The resulting polyolefins are therefore usually uniform and of one type of (statistic) microstructure. This is often advantageous for the material in a specific application, and allows one to establish relationships between the molecular structure of the precatalysts and the material properties of the polymers [3]. The latter aspect is important for producing macromolecular tailor-made materials from properly designed catalysts. In fact, the state of the art in metallocene polymerization catalysis has reached an extraordinary high level of sophistication [4] regarding the understanding of the polymerization process in many of its aspects [5], and the design and improvement of ligands for high performance catalysts, for example using models based upon molecular or quantum mechanics [6]. At the same time, a number of shortcomings arose, including (i) the often tedious multistep synthesis of precatalysts with complicated ligands, (ii) the high reactivity/oxophilicity of the (activated) complexes toward functional groups, and (iii) the unavoidable use of a large excess of costly activating reagents [7]. The latter is of particular industrial relevance because polyolefins are generally commodity products and new polyolefins with improved properties that are obtainable with metallocene catalysts tend to become very quickly commodities and thus have to compete with the established low(er) price standard polyolefins.

Therefore, the (re)discovery [8] in the last decade of the 20th century of late transition metals as polyolefin catalysts with relatively simple ligands received an im-

pressive amount of attention. Not surprising, these novel families of catalysts initiated an intense research activity in academic and industrial laboratories due to their anticipated short-term industrial application, evidenced by a steep increase in patenting activity concerning homo- and copolymerizations of ethylene and 1-olefins [9]. It not only became feasible to prepare known polyolefinic materials under even more simple conditions, but also new materials were synthesized with a molecular precision characteristic of metallocene single site catalysts. Sterically demanding diimine palladium complexes played a key role in the development of this field. In Fig. 3.1, the structure of a typical example of such a diimine catalyst precursor is shown. Here an acyl derivative is depicted, a catalyst that may also be used for the perfectly alternating copolymerization of 1-olefins and carbon monoxide [10]. The formation of polyketones exemplifies the high tolerance of the late transition metal catalysts toward functional groups, or, put differently, the higher affinity of the Lewis acid late transition metal centers for olefinic entities in comparison to heteroatom donors.

Not only palladium, but many more non-metallocene late (and early) transition metal catalysts for the coordination polymerization of ethene and 1-olefins were reported [11]. Among the most significant findings in this area are the disclosures of novel highly active and versatile catalysts based on (i) bidentate diimine [N,N] nickel and palladium complexes [12], (ii) tridentate 2,6-bis(imino)pyridyl [N,N,N] iron and cobalt complexes [13], and (iii) bidentate salicyl imine [N,O] nickel complexes [14].

Remarkably high activities for the polymerization of ethene similar to those of active Ziegler-Natta systems have been reported and the physical properties of the polyolefins produced can be tailored by the choice of the metal center and the substitution pattern of the ligand backbone [12–14]. Some of these catalytic systems are not only compatible with polar monomers, but also copolymerization of

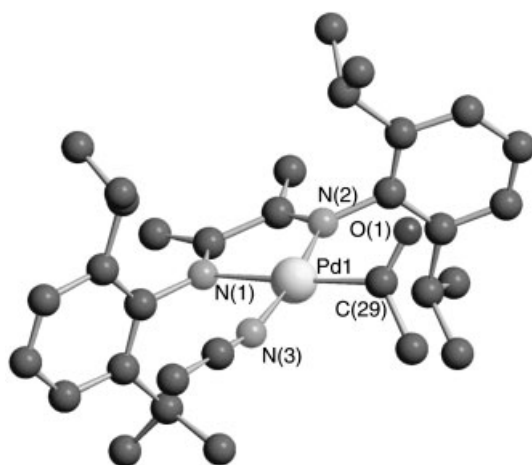
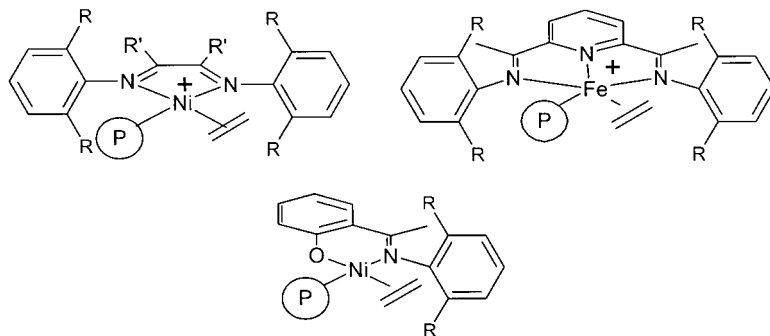


Fig. 3.1 Molecular structure of the acetonitrile adduct of mono-cationic bis(2,6-diisopropylphenyl)-2,3-dimethyl-2,3-diazabutadiene palladium acyl (tetrakis (3,5-bis(trifluoromethane)phenyl)borate as non-coordinating anion not shown). Selected bond distances (pm): Pd(1)–C(29) = 196.1(6), Pd(1)–N(1) = 215.6(4), Pd(1)–N(2) = 204.4(4), Pd(1)–N(3) = 201.0(5). Selected angles (°): N(1)–Pd(1)–N(2) = 76(6), C(29)–Pd(1)–N(3) = 98.8(2), N(1)–Pd(1)–N(3) = 95.5(2), N(2)–Pd(1)–C(29) = 98.1(2), Pd(1)–C(29)–O(1) = 121.1(5).

ethene and acrylic ester was achieved [15] and even ethene polymerization in water was observed [16].

The relatively simple reactions that lead to the chelate ligands also changed the way single site catalysts are developed. In the synthesis of ligands, application of parallel synthesis or even combinatorial methods created the opportunity to prepare ligand structures in a large variety [17]. In the same process, the complexation to metals has been optimized for performing synthesis with a high selectivity through the use of appropriate metal precursors. Furthermore, screening methods for determining catalytic activity in a high throughput fashion of the catalyst (precursors) were established.

It may now be clear that this field of olefin polymerization research is developing at an impressive and never seen pace in this area. Today, some activity-structure relationships [11–13] were experimentally established and verified in a number of theoretical studies [18, 34]. The key structural feature of the ligand framework of these catalysts is apparently sufficient steric shielding of the active cationic center to suppress undesired chain termination pathways, mostly β -hydrogen elimination and associative olefin displacements, which are intimate features of SHOP catalysts, leading to linear 1-olefins [19]. Steric shielding may, for example, be effected by the use of bulky ortho-substituted aryl groups (e.g. 2,6-diisopropylphenyl) attached to the peripheral imine nitrogen donor sites of the [N,N], [N,N,N] and [N,O] ligands (Scheme 3.1).



Scheme 3.1 Axial steric shielding in N-aryl diimine (left), bis(imino)pyridine (right) and salicyl imine (bottom) late transition metal polymerization catalysts.

Late transition metal compounds of the Group 10 with coordinated imine donor ligands were often found to yield active catalysts. In this chapter we wish to report on research carried out at or in cooperation with BASF polymer research on catalysts that carry imine donor ligands. Our objective is to introduce a number of “unusual” ligand frames for active catalysts. Unusual refers to being different to the usual condensates of alkyl-substituted anilines with aldehydes and ketones. The ligand frames that are described in the following include neutral (i) [N,N] diimine, (ii) [N,N,N] bis(imino)pyridine, monoanionic (iii) [N,O] salicyl imine, and

(iv) [N,O] ethanol imine moieties. The “unusual” imine steering groups are peripheral N-heterocyclic and electronically activating N-aryl halogen substituents. First, the synthesis of the ligands and the formation of their Fe/Co/Ni/Pd complexes are addressed. Second, we discuss the polymerization performance and the properties of the polymers and we analyze substituent effects on activity and on microstructures of the polyolefins.

3.2

Ligand and Metal Complex Synthesis

3.2.1

Diimine Systems

3.2.1.1 [N,N] Diimines Containing Peripheral N-Heteroaromatic Substituents

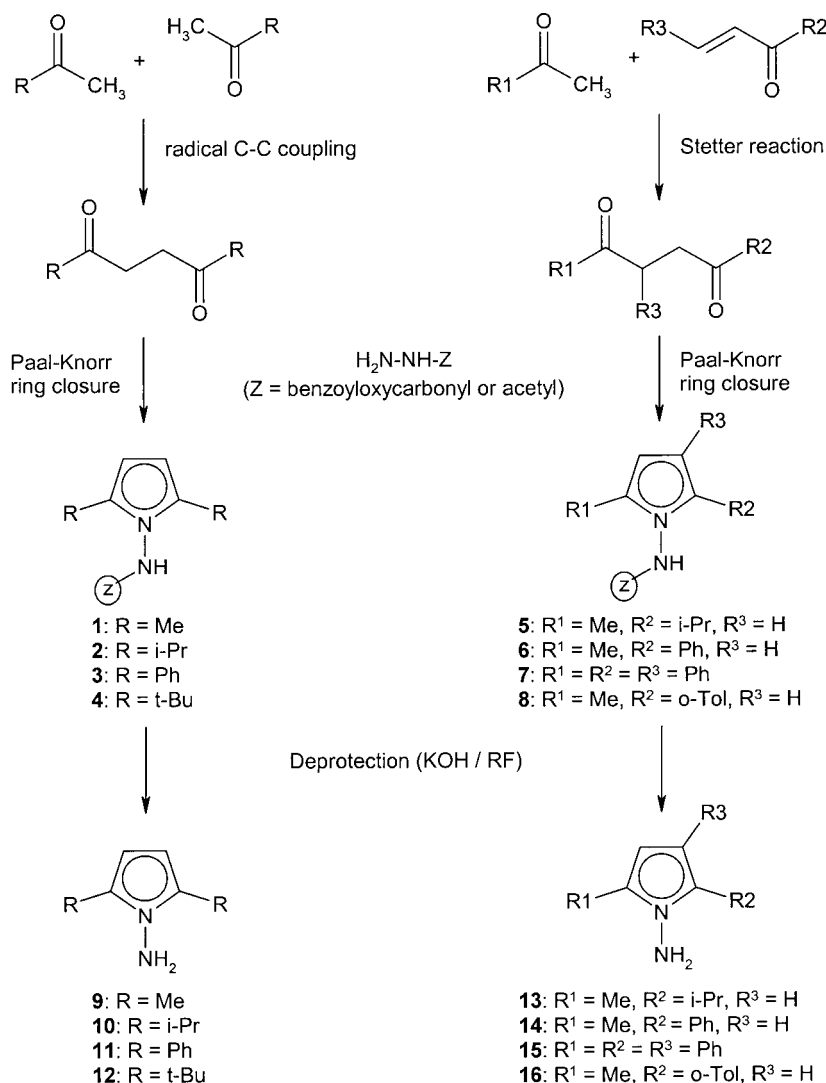
From a retrosynthetic viewpoint, N-aryl-1,2-diimine Ni precatalysts are synthesized by (i) reaction of 1,2 diimines with nickel halides from (ii) 1,2-diimine ligands which in turn are obtained by (iii) condensing 1,2-dicarbonyl substrates with two equivalents of primary aromatic amines, usually under acidic conditions [11]. In analogy, the synthesis of N-hetaryl 1,2 diimine catalysts starts from the corresponding substituted N-heterocyclic primary amines as the amine building blocks. The synthesis of three types of such heterocycles, N-amino-pyrroles, -indoles and -carbazoles, and their corresponding diimine derivatives is presented in the following sections.

Amino-pyrroles

The most general method to synthesize 2,5-disubstituted N-aminopyrroles consists of a modified Paal–Knorr condensation [20] starting from 1,4-diketones and a mono-protected hydrazine (Scheme 3.2).

The necessary symmetric 1,4-diketones may be prepared from methylketones by a copper-mediated radical C–C coupling reaction [21] (metalation of the methylketone by LDA followed by transmetalation with CuCl_2 , and thermal decomposition to the corresponding radicals with concomitant dimerization). Although the yields are rather poor, the starting materials are inexpensive and the diketones may conveniently be isolated by fractional distillation. Therefore this method is of some value. An alternative synthetic approach consists in the reaction of Grignard reagents with succinyl dichloride or alkyl succinate, respectively, catalyzed by iron(III) acetylacetonate [22] or Li_2MnCl_4 [23], but in our hands these methods were inferior to the dimerization of copper methylketones. The most versatile and useful preparation of 1,4-diketones, however, is the Stetter reaction [24]: Umpolung of aldehydes with cyanide or with N-heterocyclic carbenes followed by reaction with vinyl ketones allows the convenient one-pot preparation of symmetric and unsymmetric 1,4-diketones on a large scale (>20 g).

Paal-Knorr condensation of these 1,4-diketones with protected hydrazines gives access to the corresponding N-protected N-aminopyrroles 1–8 in a simple proce-



Scheme 3.2 Synthesis of N-aminopyrroles **9–16** (Me=methyl, i-Pr=isopropyl, Ph=phenyl, t-Bu=*t*-butyl, o-Tol=*ortho*-tolyl).

ture. In contrast to the reported protocol which uses rather exotic protecting groups [$\text{Cl}_3\text{CCH}_2\text{OC(O)}$, $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{OC(O)}$] [20], we used the more common protecting group benzyloxycarbonyl or acetyl, respectively. In terms of yield of products the benzyloxycarbonyl group (**1–4**: 66–89% yield) is preferred over the acetyl group (**5–6**: 37–53% yield), but in the following deprotection step the acetyl moiety is easier to cleave off.

The N-aminopyrroles **9–16** were obtained from these amides in 80–95% yield by alkaline hydrolysis (1–36 h) with a KOH saturated refluxing ethylene glycol solution. This convenient but rather drastic deprotection protocol shows that N-aminopyrroles are quite stable compounds. The high stability of aminopyrroles **9–16** presumably results from the fact that both α -positions are blocked in these 2,5-disubstituted pyrroles. The parent member of this family of compounds, unsubstituted N-aminopyrrole, is the only commercially available N-amino-azole. Ironically, it is also the least stable compound in the series.

In summary, N-amino-2,5-disubstituted pyrroles with a range of substituents can be conveniently prepared on a large scale. The only limitation of the method is the commercial availability of the starting 1,4-diketones. They in turn are most easily prepared from the Stetter condensation.

N-Amino-indoles and -carbazoles

To further extend the substitution pattern of these building blocks, benzannulated N-amino-N-heterocycles were prepared: Electrophilic amination of indole, 2-methylindole, or carbazole using hydroxylamine-O-sulfonic acid [25] yielded the corresponding N-amino-indole **17**, -2-methylindole **18**, and -carbazole **19**, respectively. However, attempting the same reaction with 2,7-dimethylindole or dibenzazepine (iminostilbene) failed, most likely due to steric hindrance.

Thus eleven N-amino-N-heterocycles were synthesized. Together with the commercially available unsubstituted N-amino-pyrrole, twelve different N-amino-azoles became available as ligand precursor. Their properties – with regard of their intended use as steering groups in the ligand backbone of the olefin polymerization catalysts – differ in terms of steric bulk of the substituents, symmetry, and electronic properties, as can be seen from inspecting Chart 3.1.

3.2.1.2 1,2-Diimine Ligands with N-Hetaryl Substituents

Two methods of imine formation were employed (Scheme 3.3) to condense the N-hetaryl building blocks with 1,2-diketones.

Either a standard procedure in methanol with formic acid as catalyst or a trimethylaluminum promoted [26] condensation was found effective. The latter method is an extremely efficient protocol that effects the imination through sequential hemiaminal and amination followed by elimination of tetramethylaluminumoxane. This method is of great value for this chemistry because sterically or electronically unfavorable dicarbonyl substrates may be converted with ease into the corresponding 1,2-diimine ligands in good yields (approximately 70%) and in a short reaction period (a few minutes to hours, depending on the steric bulk of the starting dione and/or amine component). As noted in the introduction, steric control or axial shielding is one of the most important aspects in the ligand design of these 1,2-diimine catalysts, therefore a reliable general ligand synthesis route is crucial for optimizing the performance of the catalyst constitution.

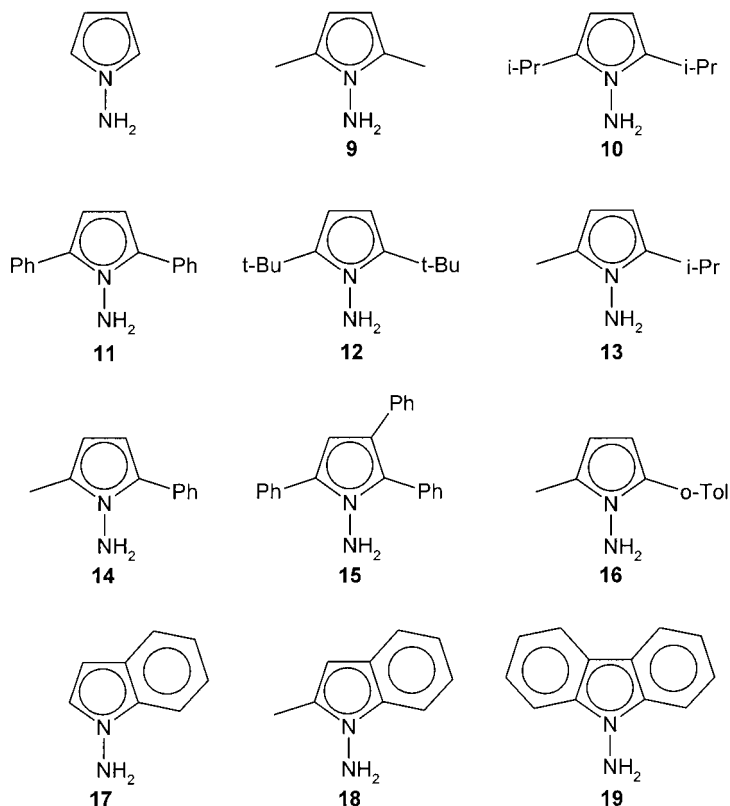


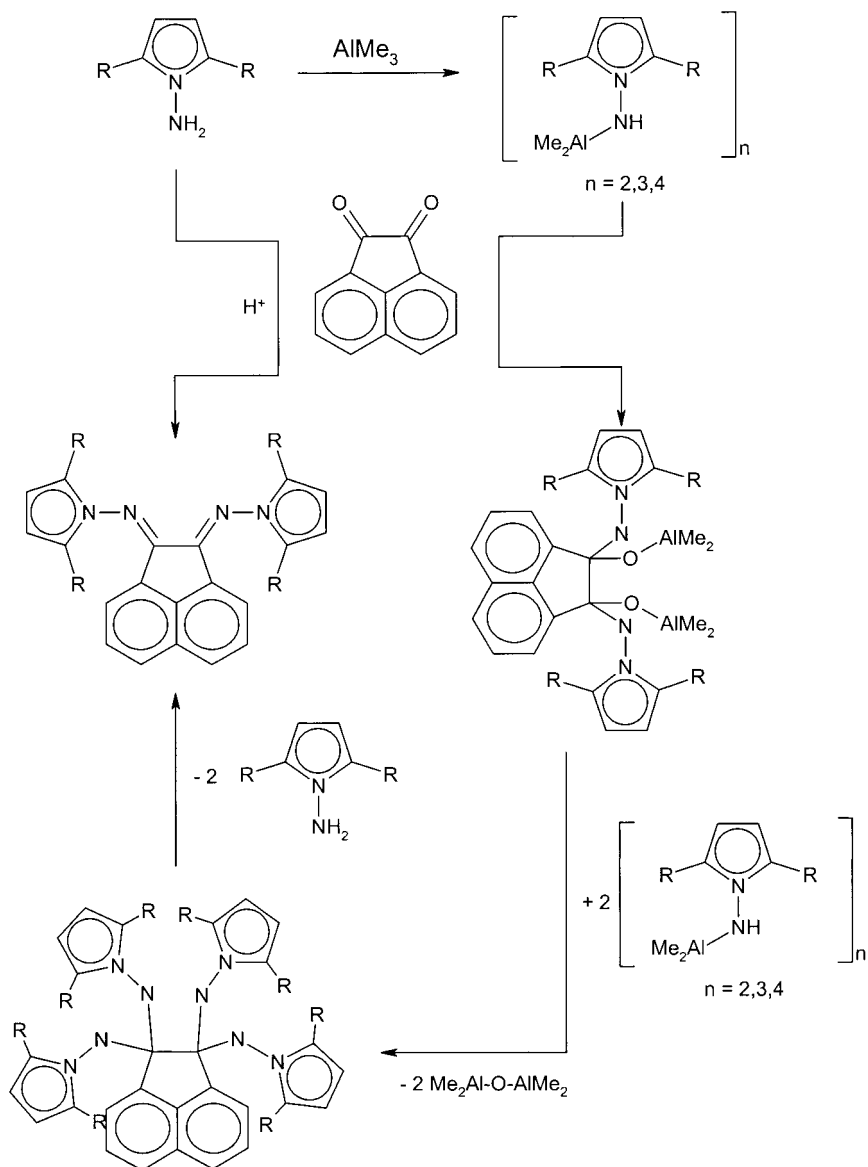
Chart 3.1 Overview of N-amino azole building blocks.

A set of nine ligands **20–28** based on the rigid acenaphthenequinone backbone containing N–N bonded peripheral substituents were synthesized (Chart 3.2). Variations include the 2,5-substitution pattern of pyrrole and the degree of annelation. In addition, one example of a “mixed” ligand with one N-pyrrolyl and one N-aryl substituent was obtained. All these compounds are yellow or red air-stable solids with spectroscopic properties in line with their structural features.

3.2.1.3 Nickel Complexes with N-Hetaryl 1,2-Diimine Ligands

Reaction of ligands **20–28** with one equivalent of (dimethoxyethane)NiBr₂ under inert conditions affords the corresponding (diimine)NiBr₂ complexes **29–37** in good yield (Chart 3.3).

They are air-stable as solids, but slightly air-sensitive in solution and thermally very stable (without a detectable melting point up to 200°C). The highly colored (dark brown) and paramagnetic compounds are fairly polar and therefore only slightly soluble in common organic apolar solvents. Therefore, spectroscopic char-



Scheme 3.3 Synthesis of 1,2 diimines by H^+ -catalyzed or Al-assisted condensation of 1,2-diones and aminoazoles.

acterization does not give very meaningful data, for example no informative NMR spectra could be obtained since only very broad signals are observed. Fig. 3.2 shows the results of an X-ray single structure analysis of compound 37.

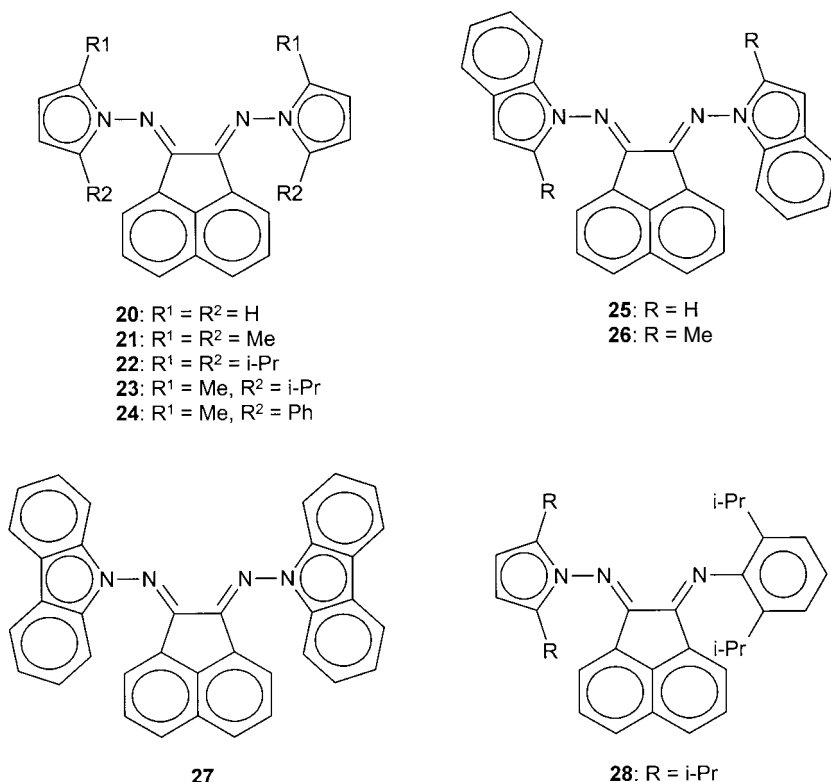


Chart 3.2 1,2-Diimine ligands **20–28**.

In the solid state, complex **37** exists as a dimer with a central inversion center. Two molecules are bridged by two bromo ligands, leaving one terminal bromo ligand at a five-coordinated Ni center. The coordination sphere of Ni is essentially square pyramidal. The peripheral N-substituents are roughly orthogonal to the Ni-acenaphthoquinone diimine backbone, effecting axial steric shielding of the Ni atom. Fig. 3.3 shows a view of the core part of the molecule. The orthogonality of the N-substituents and the steric similarity between N-2,6-diisopropylphenyl and N-2,5-diisopropylpyrrolyl groups as peripheral steering ligands is easily appreciated. Hence there is no major structural difference between N-aryl and N-hetaryl Ni-diimine complexes, in accord with the design principle of this family of precatalysts.

3.2.1.4 Diimine Nickel and Palladium Complexes with 2,6-Dibromo-4-methylphenyl Groups

Another appealing steric congruence exists between 2,6-diisopropylphenyl and 2,6-dibromophenyl groups (Fig. 3.4). Note though that the isopropyl group has quite different dynamics.

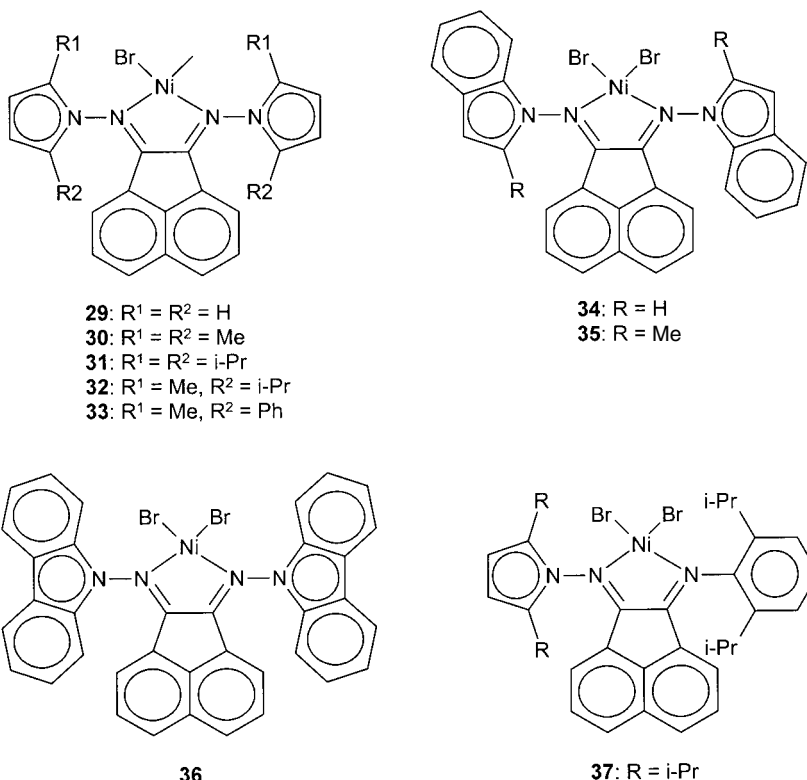


Chart 3.3 [N,N] nickel complexes 29–37.

As was already mentioned, the nickel and palladium compounds that greatly influenced the development of alternative single site catalysts for ethene polymerization carry diimine ligands with 2,6-diisopropylphenyl groups. Here the palladium derivative is of particular interest because it polymerizes ethene to a highly branched product with a low glass temperature. Such materials could be applied as low temperature impact modifiers. However, the catalytic activity is not particularly high. We wanted to improve the catalytic properties by enhancing the Lewis acidity of the palladium center, and – for obvious reasons – not change the sterics in a major way (*vide supra*).

The diimine **38** from 2,3-butanedione (diacetyl) and 2,6-dibromo-4-methylaniline was prepared by refluxing the starting materials in toluene under dynamic removal of the azeotrope (Scheme 3.4).

A simple acid-catalyzed condensation in methanol such as for 2,6-diisopropylaniline yielded no product. Another difference in behavior between this diimine and the one based upon 2,6-diisopropylaniline is observed in the reaction with (COD)PdCl₂ or (COD)PdMeCl: 2,3-bis(2,6-dibromo-4-methylphenyl)imine butane is inert toward these palladium catalyst precursors, whereas the alkyl-substituted

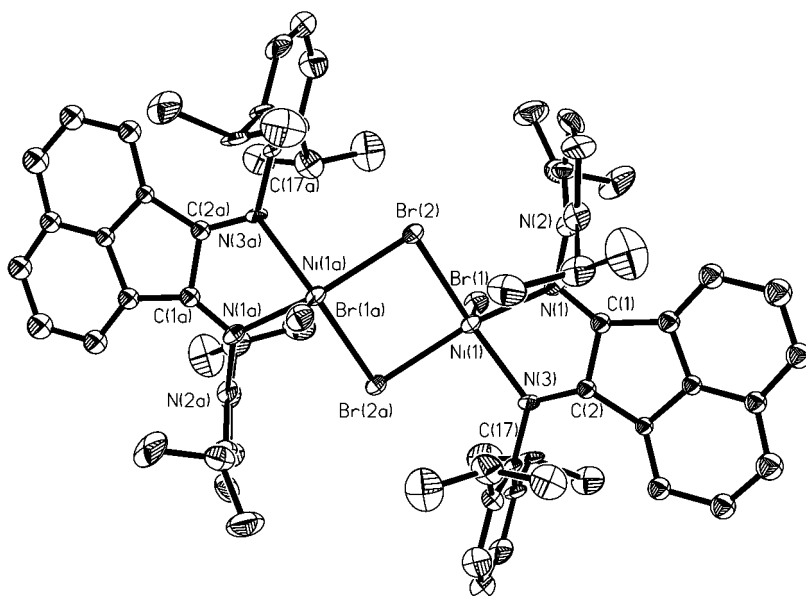


Fig. 3.2 Molecular structure of nickel complex **37**; hydrogen atoms are omitted for clarity. Selected bond distances (pm):

Ni(1)–Br(1) = 240.9(2), Ni(1)–Br(2) = 250.9(2),
Ni(1)–N(1) = 209.6(11), Ni(1)–N(3) =
213.1(10), N(1)–N(2) = 144.0(13),
N(1)–C(1) = 125.8(14), C(1)–C(2) = 150(2),

N(3)–C(2) = 129.6(14), N(3)–C(17) = 142.6(14).

Selected angles (°): Br(1)–Ni(1)–Br(2) =
106.18(8), Br(1)–Ni(1)–Br(2a) = 103.78(9),
Ni(1)–Br(2)–Ni(1a) = 91.97(7), N(1)–Ni(1)–
Br(2) = 89.9(3), N(3)–Ni(1)–Br(2a) = 93.4(3),
N(1)–Ni(1)–N(3) = 78.5(4).

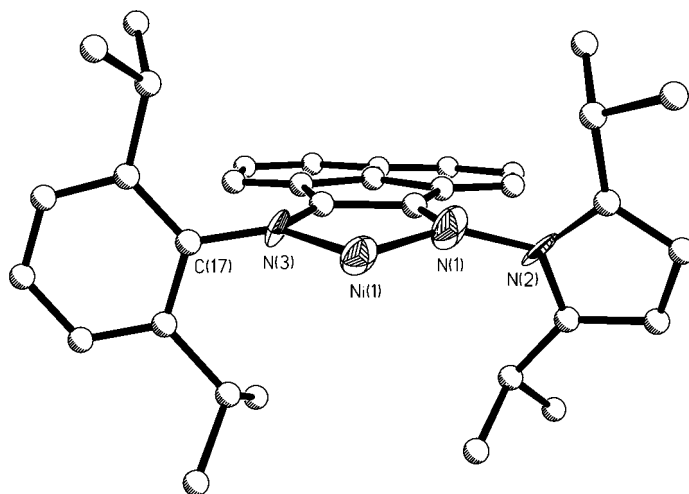


Fig. 3.3 View of nickel complex **37** showing the orthogonal N-2,6-diisopropylpyrrolylphenyl and N-2,5-diisopropylpyrrolyl groups with respect to the ligand backbone [Ni₂Ni] plane.

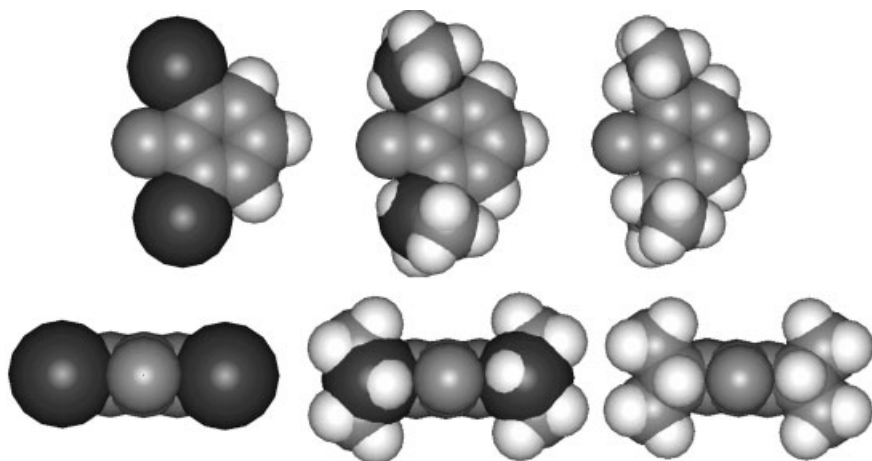
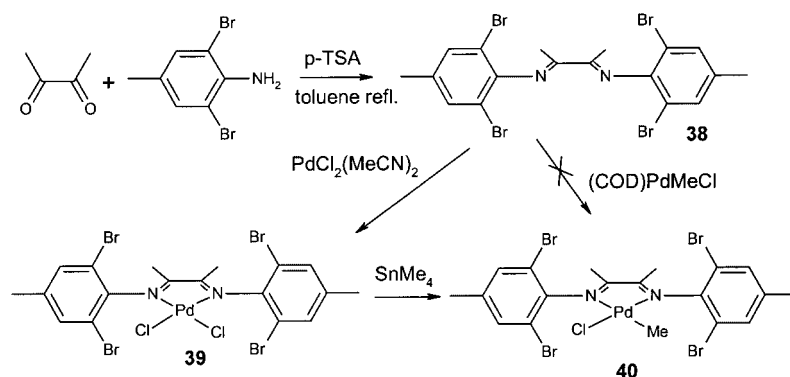


Fig. 3.4 Steric extension of 2,6-dibromo- (left), 2,6-diisopropyl-aniline (right) and overlay, front and side views.



Scheme 3.4 Synthesis of N,N-[2,3-bis(2,6-dibromophenylimine butane)]palladium dichloride.

phenyl diimines readily react to give a catalyst precursor. However, the bisacetoni-trile adduct of palladium dichloride reacted cleanly with **38** and the resulting (N,N)PdCl₂ (**39**) was characterized by single crystal X-ray diffraction (Fig. 3.5). This compound was methylated with tetramethylstannane to give the mono-methyl palladium derivative **40**. For the alkylation to proceed, tetramethylammo-nium chloride was added as a catalyst [27].

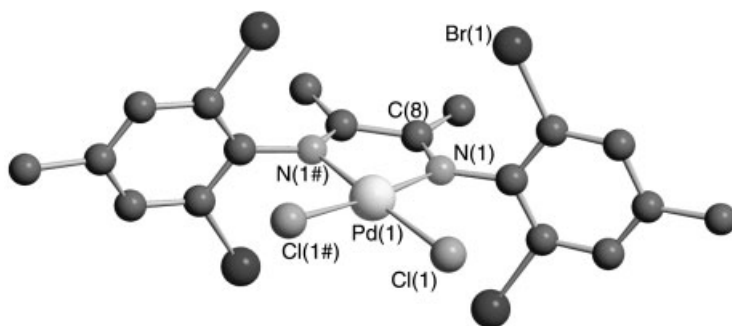


Fig. 3.5 Structure of N,N-[2,3-bis(2,6-dibromo-4-methylphenylimino)butane]palladium dichloride **39**. Pd(1)–N(1) = 203.3(9) pm, Pd(1)–Cl(1) = 230.0(3) pm, N(1)–C(8) =

132.4(12) pm; (diimine plane NCCN, aryl) = 94.1°, N(1)–Pd(1)–N(1#) = 79.2(5)°, N(1)–Pd(1)–Cl(1) = 95.5(3)°, N(1)–Pd(1)–Cl(1#) = 174.3(3)°.

3.2.2

Diimine Pyridine Systems

3.2.2.1 [N,N,N] Bis(imino)pyridine Iron and Cobalt Complexes with Peripheral N-Heteroaromatic Substituents

Retrosynthetically, preparation of N-azolyl 2,6-bis(imino)pyridyl metal complexes as precatalysts for polymerization involves (i) synthesis of N-amino azoles, (ii) condensation of 2,6-diacetylpyridine with two equivalents of N-amino azole, and (iii) complexation of the appropriate transition metal halide with the tridentate ligands. The latter two reactions present no real challenge and are more or less analogous to the published preparation of N-aryl 2,6-bis(imino)pyridyl complexes [13], and the more demanding synthesis of N-amino-azoles was covered in a preceding section.

N-Azolyl-Containing Tridentate Ligands and their Fe/Co Complexes

The bis(imino)pyridyl ligands are easily synthesized by reaction of 2,6-diacetylpyridine with two equivalents of the heterocyclic amine; these condensations were performed under acidic conditions, either in methanolic solution with catalytic amounts of formic acid or in refluxing propionic acid in the case of less reactive components. In this manner, twelve different [N,N,N] bis(imino)pyridyl ligands (41–52) were prepared (Chart 3.4).

Attempting the condensation between 2,5-di-*t*-butyl-N-aminopyrrole **12** and 2,6-diacetylpyridine met with failure, indicating that the two very bulky *t*-butyl substituents are not compatible with the [N,N,N] ligand framework. Whereas all the ligands 41–51 are symmetric in terms of bearing the same N-azolyl moiety on the two imine nitrogens, one example of an asymmetric ligand with different N-substituents (**52**) was prepared by first condensing one equivalent of N-aminocarbazole to afford the corresponding monoimine which was reacted in a second step with N-aminopyrrole **10**. In general, in all these condensations the mono imine was formed very quickly whereas the second imination proceeded much slower.

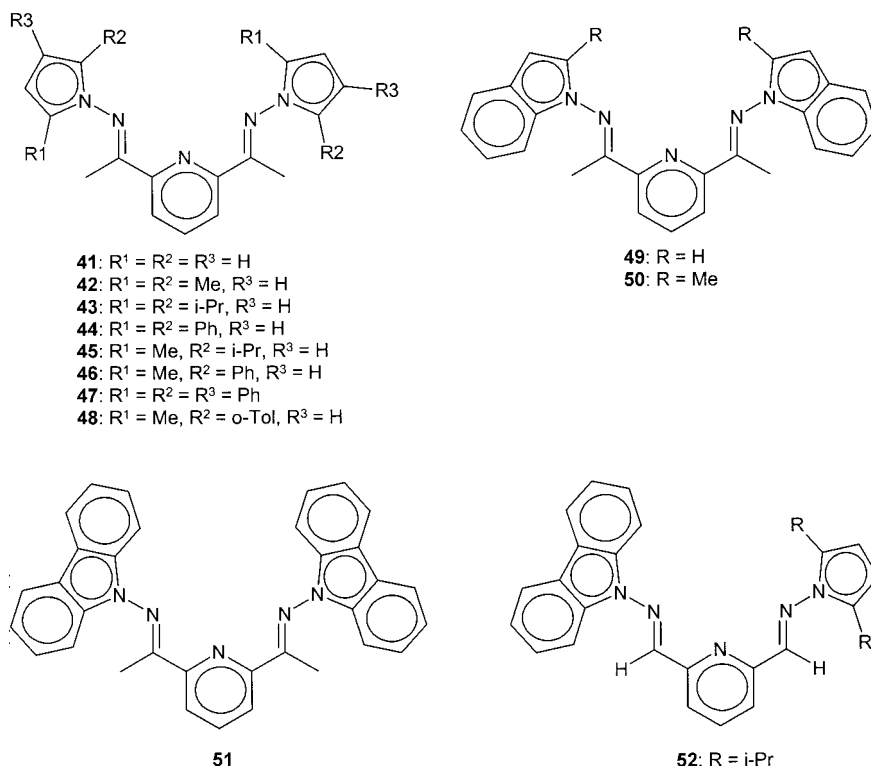


Chart 3.4 [N,N,N] ligands 41–52.

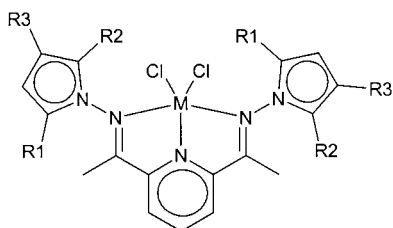
The complexes **53a–62a** (Chart 3.5) were synthesized in good yield from the ligands 41–52 by reaction with the appropriate metal halides ($FeCl_2$, $CoCl_2$, $FeCl_3$).

Almost all of the pyrrole-, indole-, and carbazole-containing systems afforded stable Fe(II) and Co(II) complexes. The only exceptions are ligands 44 and 47 which contain only aryl substituents. This indicates that two pairs of *o*-phenyl groups on the N-pyrrolyl substituents impose too much of a steric hindrance and/or are too electron-withdrawing for the corresponding [N,N,N] metal complex to form. The two Fe(III) precatalysts **54c**, **55c** were synthesized to evaluate the dependence of the polymerization performance on the oxidation state of the metal center. In total, twenty-one different N-azolyl complexes were prepared aiming at a thorough structure–activity evaluation (*vide infra*).

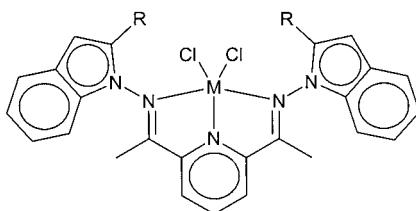
All complexes **53a–62a** are paramagnetic, deeply colored, mostly dark green for Fe(II) and dark brown for Co(II). They are thermally very stable, no melting or decomposition is observed up to 300 °C. These properties are parallel to those of Gibson's and Brookhart's N-aryl bis(imino)pyridyl complexes [13].

For one representative of this family of precatalysts (**61a**) suitable single crystals for an X-ray structure analysis were obtained. Fig. 3.6 shows the molecular structure of Fe(II) complex **61a**.

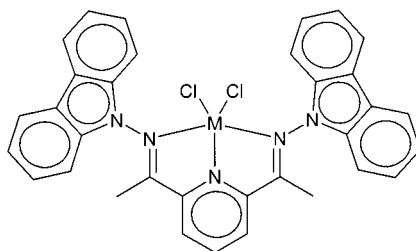
Chart 3.5 [N,N,N] iron (a) and cobalt (b) complexes **53–62a**.



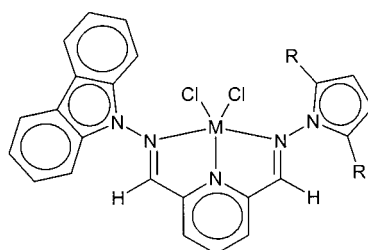
- 53:** $R^1 = R^2 = R^3 = H$; **53a:** $M = Fe(II)$; **53b:** $M = Co(II)$
54: $R^1 = R^2 = Me$, $R^3 = H$; **54a:** $M = Fe(II)$; **54b:** $M = Co(II)$; **54c:** $M = Fe(III)Cl$
55: $R^1 = R^2 = i\text{-Pr}$, $R^3 = H$; **55a:** $M = Fe(II)$; **55b:** $M = Co(II)$; **55c:** $M = Fe(III)Cl$
56: $R^1 = Me$, $R^2 = i\text{-Pr}$, $R^3 = H$; **56a:** $M = Fe(II)$; **56b:** $M = Co(II)$
57: $R^1 = Me$, $R^2 = Ph$, $R^3 = H$; **57a:** $M = Fe(II)$; **57b:** $M = Co(II)$
58: $R^1 = Me$, $R^2 = o\text{-Tol}$, $R^3 = H$; **58a:** $M = Fe(II)$; **58b:** $M = Co(II)$



- 59a:** $R = H$, $M = Fe(II)$
59b: $R = H$, $M = Co(II)$
60a: $R = Me$, $M = Fe(II)$
60b: $R = Me$, $M = Co(II)$



- 61a:** $M = Fe(II)$
61b: $M = Co(II)$



- 62a:** $R = Me$, $M = Fe(II)$

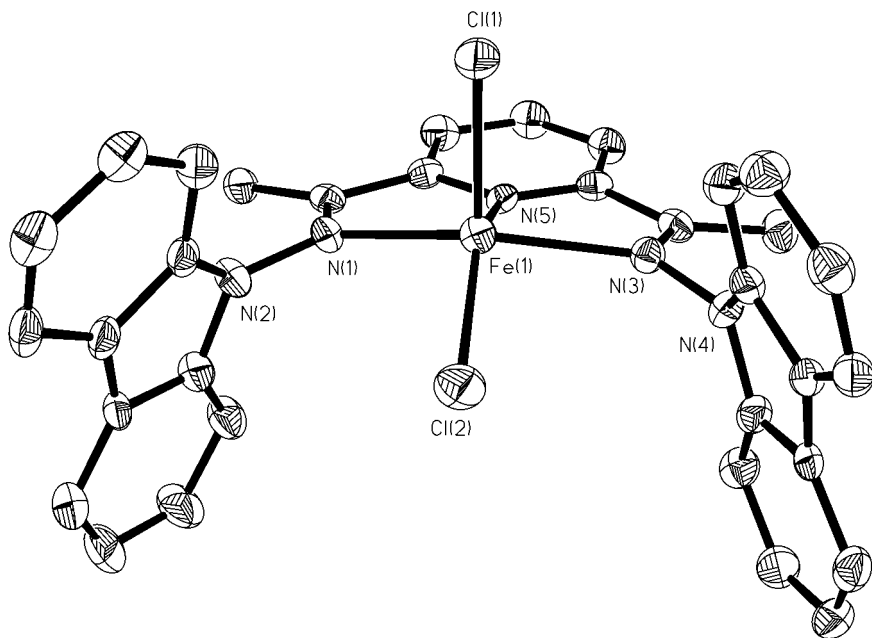


Fig. 3.6 Molecular structure of iron complex **61a**; hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (pm): Fe(1)–N(1) = 220.2(4), Fe(1)–N(3) = 222.2(4), Fe(1)–N(5) = 207.9(5), Fe(1)–Cl(1) = 230.9(2), Fe(1)–Cl(2) = 225.9(2), N(1)–N(2) = 140.3(6), N(3)–N(4) = 141.8(6). Selected an-

gles ($^{\circ}$): N(1)–Fe(1)–N(5) = 73.5(2), N(3)–Fe(1)–N(5) = 73.0(2), N(1)–Fe(1)–N(3) = 143.1(2), N(5)–Fe(1)–Cl(1) = 96.69(12), N(3)–Fe(1)–Cl(1) = 100.12(12), N(1)–Fe(1)–Cl(1) = 98.56(12), N(5)–Fe(1)–Cl(2) = 138.67(12), N(3)–Fe(1)–Cl(2) = 95.66(13), N(1)–Fe(1)–Cl(2) = 99.47(13).

The metal is coordinated in a distorted trigonal bipyramidal geometry to the three nitrogens N(1), N(3), N(5) of the bis(imino)pyridyl ligand and to two chlorines; furthermore the metal is clearly displaced from the [N,N,N] ligand plane by 40.6(4) pm. The bond distance of the pyridyl nitrogen is significantly shorter than the distances of both imino nitrogens and the two chlorine substituents have more or less similar metal-chlorine bond lengths. The planes of the sterically shielding N-carbazolyl groups are roughly orthogonal to the plane of the [N,N,N] bis(imino)pyridyl ligand backbone [$78.5(3)^{\circ}$ and $75.1(2)^{\circ}$] and the N-carbazolyl moieties are planar in accordance with the sp^2 hybridization of the nitrogens N(2), N(4) in these N-heterocycles. All these structural features of **61a** are quite similar to those of Gibson's N-aryl bis(imino)pyridyl complexes [13], again indicating only subtle structural differences between N-azolyl and N-aryl bis(imino)pyridyl metal halide precatalysts.

Tab. 3.1 ^1H NMR shifts of diimine pyridine ligands **63–65** and iron complexes **66**, **67**, **69** in CD_2Cl_2 (relative to solvent at $\delta=5.25$ ppm).

Imine sub.	<i>p</i> -pyr	<i>m</i> -pyr	<i>CMe</i>	<i>m</i> -Aryl	<i>o</i> -Aryl	<i>p</i> -Aryl
A: Ligands						
Me_2 63a	7.90	8.50	2.25	7.05	2.04	6.93
iPr_2 65a	7.92	8.45	2.25	7.12	2.75, 1.13	7.12
Br_2, Me 64	7.93	8.51	2.33	7.39		2.31
Br_3 65	7.95	8.50	2.33	7.72		
Cl_2 63	7.96	8.53	2.37	7.37		7.01
B: [N,N,N] Iron dichloride complexes						
iPr_2 69	79.1	79.5	−36.3	14.6	−21.5/−5.5	−10.3
Br_2, Me 67	48.5	81.9	−28.7	18.0		24.2
Cl_2 66	42.8	81.0	−25.4	18.3		−11.1

3.2.2.2 N-Halogenoaryl-Containing Tridentate Ligands and their Fe Complexes

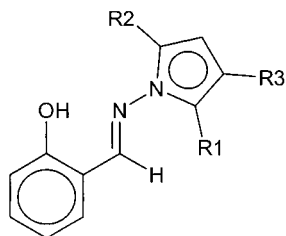
The synthesis of pyridine imines on the basis of 2,6-dichloro- (**63**), 2,6-dibromo-4-methyl- (**64**) and 2,4,6-tribromoaniline (**65**) was successful through reaction of 2,6-diacetylpyridine with the anilines in refluxing benzene and dynamically removing the water formed. The condensation with the electron-poor anilines is not particularly fast, but after two weeks enough product is present to allow their isolation by column chromatography. Complexation of **63–65** to iron(II)chloride was achieved in a fast and quantitative reaction by combining iron dichloride tetrahydrate with the ligands in butanol or THF. Reaction is fast and quantitative to give the usual blue complexes (Tab. 3.1). In addition, diimine pyridine iron dichloride complexes were prepared on the basis of 2,6-dimethyl (**68**) and 2,6-diisopropylaniline (**69**). The proton chemical shifts of these paramagnetic compounds become easily assignable by mutual comparison.

3.2.3

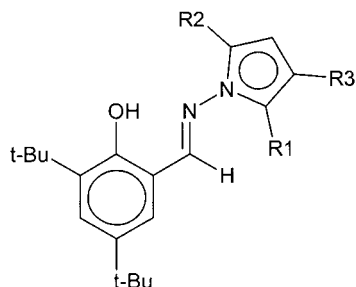
Salicylimine Systems

3.2.3.1 [N,O] Salicylimine Nickel Complexes Containing Peripheral N-Heteroaromatic Substituents

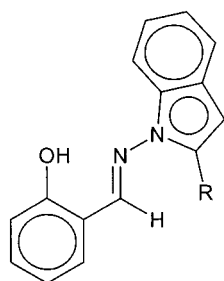
Salicylaldimine ligands are in general synthesized by condensation of amines with salicyl aldehydes. Quite similarly, using N-amino-azoles **9–19** as the amine component affords under standard condensation conditions (alcoholic solvent, protic catalysis, reflux) [N,O] ligands **70–85** in 15–90% yield. The yield is dependent on the steric bulk of the substituted N-amino-N-heteroaromatic group. Two series of ligands were synthesized, one with additional *t*-butyl substituents (**78–85**) to introduce more steric bulk in the ligand frame and those (**70–77**) without substituents on the salicyl backbone (Chart 3.6). All these ligands are stable, yellow compounds which show spectroscopic properties consistent with their structure.



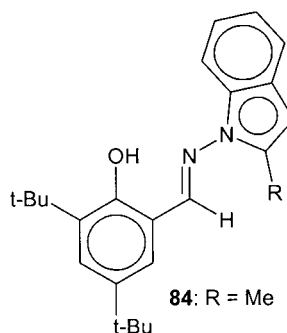
- 70:** $R^1 = R^2 = \text{Me}, R^3 = \text{H}$
71: $R^1 = R^2 = \text{Ph}, R^3 = \text{H}$
72: $R^1 = \text{Me}, R^2 = i\text{-Pr}, R^3 = \text{H}$
73: $R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$
74: $R^1 = \text{Me}, R^2 = o\text{-Tol}, R^3 = \text{H}$
75: $R^1 = R^2 = R^3 = \text{Ph}$



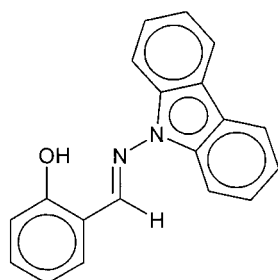
- 78:** $R^1 = R^2 = \text{Me}, R^3 = \text{H}$
79: $R^1 = R^2 = \text{Ph}, R^3 = \text{H}$
80: $R^1 = \text{Me}, R^2 = i\text{-Pr}, R^3 = \text{H}$
81: $R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$
82: $R^1 = \text{Me}, R^2 = o\text{-Tol}, R^3 = \text{H}$
83: $R^1 = R^2 = R^3 = \text{Ph}$



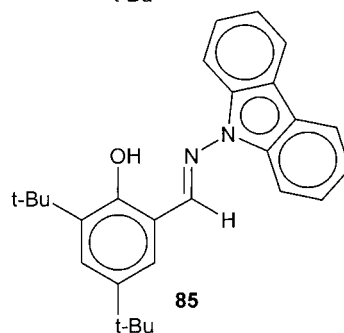
76: $R = \text{Me}$



84: $R = \text{Me}$



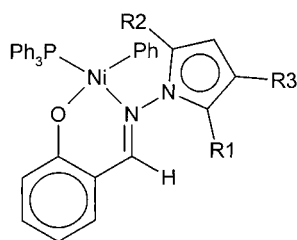
77



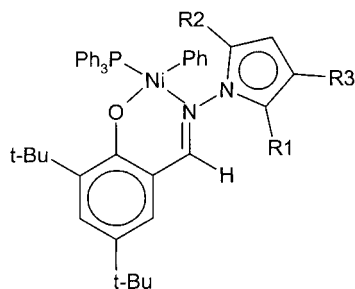
85

Chart 3.6 [N,O] ligands **70–85**.

Synthesis of the corresponding neutral [N,O] Ni complexes **86–101** is accomplished by deprotonation with *n*-butyllithium followed by reaction with bis(triphenylphosphine)phenyl(chloro)nickel [28] (Chart 3.7). Complexes **86–101** are orange solids which are slightly air-sensitive and moderately paramagnetic due to a small tetrahedral distortion of the square planar coordination. However, ^1H and ^{31}P -NMR gave usually well-resolved spectra, whereas in the ^{13}C -NMR spectra only in a number of cases useful information could be obtained.



- 86:** $R^1 = R^2 = \text{Me}, R^3 = \text{H}$
87: $R^1 = R^2 = \text{Ph}, R^3 = \text{H}$
88: $R^1 = \text{Me}, R^2 = i\text{-Pr}, R^3 = \text{H}$
89: $R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$
90: $R^1 = \text{Me}, R^2 = o\text{-Tol}, R^3 = \text{H}$
91: $R^1 = R^2 = R^3 = \text{Ph}$



- 94:** $R^1 = R^2 = \text{Me}, R^3 = \text{H}$
95: $R^1 = R^2 = \text{Ph}, R^3 = \text{H}$
96: $R^1 = \text{Me}, R^2 = i\text{-Pr}, R^3 = \text{H}$
97: $R^1 = \text{Me}, R^2 = \text{Ph}, R^3 = \text{H}$
98: $R^1 = \text{Me}, R^2 = o\text{-Tol}, R^3 = \text{H}$
99: $R^1 = R^2 = R^3 = \text{Ph}$

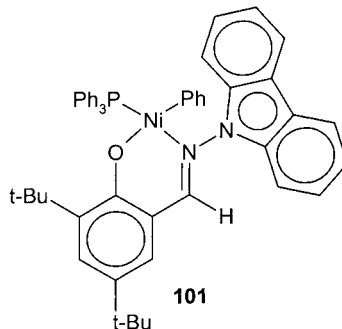
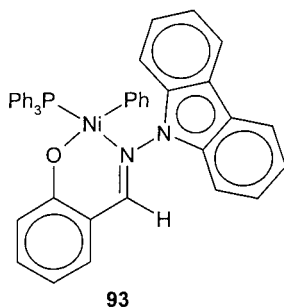
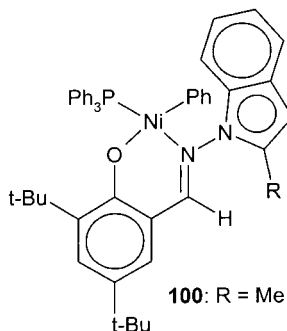
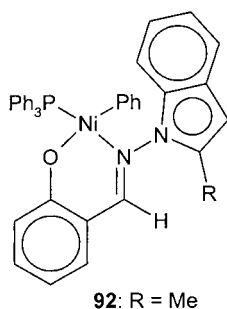


Chart 3.7 [N,O] nickel complexes **86–101**.

Figs 3.7 and 3.8 show the X-ray crystal structures of **90** and **91**, respectively. Overall, both structures show the expected square planar coordination geometry around the nickel center with more or less orthogonal peripheral N-pyrrolyl and Ni-phenyl substituents. The different axial steric shielding of the metal center by the differently substituted pyrrolyl groups of complexes **90** and **91** is easily appreciated.

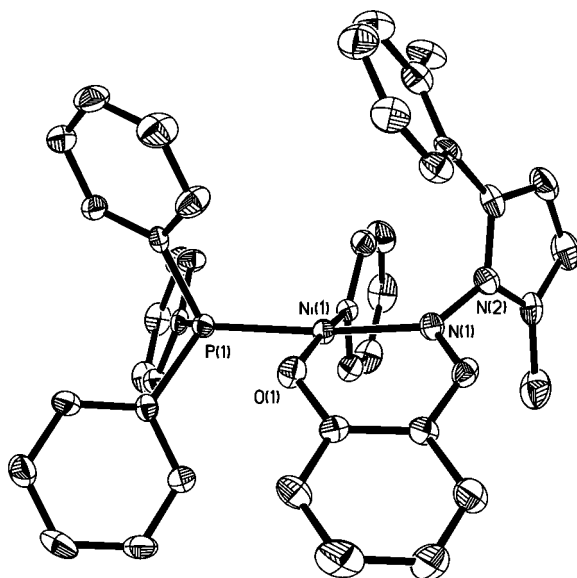


Fig. 3.7 Molecular structure of nickel complex **90**; hydrogen atoms are omitted for clarity. Selected bond distances (pm): Ni(1)–O(1)=187.5(4), Ni(1)–C(30)=188.8(5), Ni(1)–N(1)=193.3(4), Ni(1)–P(1)=218.5(2), N(1)–N(2)=141.8(6). Selected angles (°): N(1)–

Ni(1)–P(1)=177.60(13), O(1)–Ni(1)–C(30)=174.28(19), P(1)–Ni(1)–O(1)=88.35(12), P(1)–Ni(1)–C(30)=85.98(16), N(1)–Ni(1)–O(1)=91.74(17), N(1)–Ni(1)–C(30)=93.89(20).

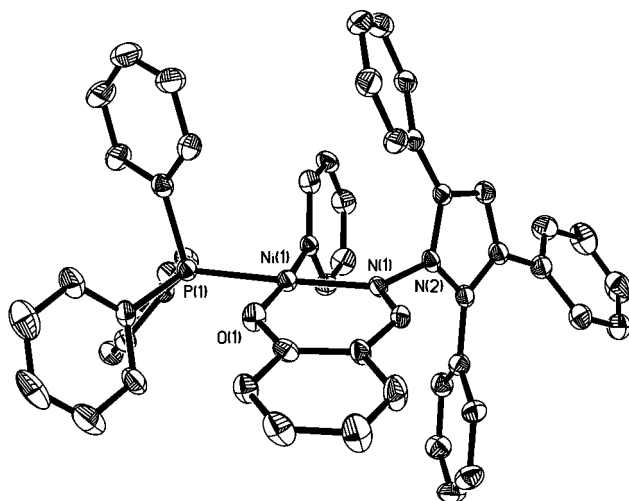


Fig. 3.8 Molecular structure of nickel complex **91**; hydrogen atoms are omitted for clarity. Selected bond distances (pm): Ni(1)–O(1)=190.2(4), Ni(1)–C(1)=189.1(6), Ni(1)–N(1)=192.6(5), Ni(1)–P(1)=217.3(2), N(1)–

N(2)=140.4(6). Selected angles (°): N(1)–Ni(1)–P(1)=173.5(2), O(1)–Ni(1)–C(1)=170.7(2), P(1)–Ni(1)–O(1)=87.49(13), P(1)–Ni(1)–C(1)=89.6(2), N(1)–Ni(1)–O(1)=90.8(2), N(1)–Ni(1)–C(1)=93.0(2).

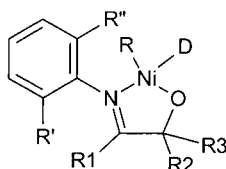
3.2.4

Ethanol Imine Ligands and their Nickel Complexes

Thus far we have dealt with variations of ligands with frames of known catalytically active late transition metal compounds. In general, single site catalysts with late transition metal compounds carry neutral or monoanionic mono-, bi- or tridentate ligands with P, N and/or O (S) donor atoms [8c, 19]. Active nickel catalysts may be obtained with anionic chelating ligands that contain P,O- and N,O-frames that build 5- and 6-membered metallacycles. 2-Alkoxyimines constitute a type of anionic bidentate ligand frame that has not been considered up to now as a possible alternative to established systems. They combine the anionic alkoxy and a neutral imine entity, reminiscent of alkoxy and phosphane coordination sites in the SHOP olefin oligomerization catalysts [8, 29]. The alkoxyimine ligands have three domains where substituents may be varied easily. These are the phenyl imine ortho positions and the imine and the hydroxy carbon atom substituents (Chart 3.8).

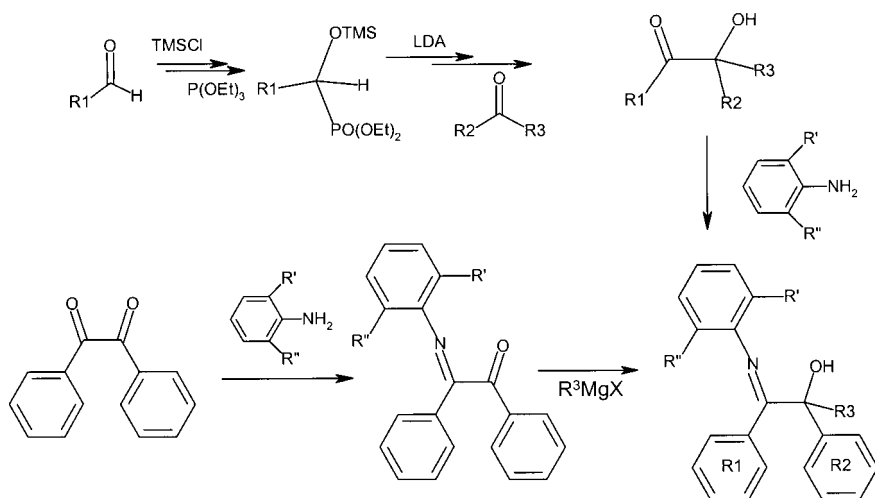
They are prepared from readily available starting materials along well-established reaction pathways (Scheme 3.5).

The first route uses benzoin derivatives as intermediates. These become available from 1-trimethylsilyloxyphosphonates, which are prepared from aldehydes in an one-pot procedure. The phosphonates are then transformed into benzoins



- 102:** R¹, R², R³ = Ph, Me, Me; R', R'' = Me, Me; **117:** R = Ph, D = PPh₃
103: R¹, R², R³ = Ph, Me, Me; R', R'' = Me, Et; **118:** R = Ph, D = PPh₃
104: R¹, R², R³ = Ph, Me, Me; R', R'' = iPr, iPr; **126:** R = Me, D = CH₂=PPh₃
105: R¹, R², R³ = Ph, Ph, H; R', R'' = H, H; **119:** R = Ph, D = PPh₃
106: R¹, R², R³ = Ph, Ph, H; R', R'' = Me, Me; **120:** R = Ph, D = PPh₃
107: R¹, R², R³ = Ph, Ph, H; R', R'' = Me, Et; **121:** R = Ph, D = PPh₃
108: R¹, R², R³ = Ph, Ph, Me; R', R'' = H, H; **122:** R = Ph, D = PPh₃
109: R¹, R², R³ = Ph, Ph, Me; R', R'' = Me, Me; **127:** R = Me, D = CH₂=PPh₃
109: R¹, R², R³ = Ph, Ph, Me; R', R'' = Me, Me; **123:** R = Ph, D = PPh₃
110: R¹, R², R³ = m-tol, m-tol; Me, R', R'' = Me, Me; **124:** R = Ph, D = PPh₃
111: R¹, R², R³ = Ph, Ph, Me; R', R'' = iPr, iPr; **125:** R = Ph, D = PPh₃
112: R¹, R², R³ = Ph, Ph, iPr; R', R'' = Me, Me;
113: R¹, R², R³ = Ph, Ph, Ph; R', R'' = iPr, iPr; **128:** R = Me, D = CH₂=PPh₃
114: R¹, R², R³ = Ph, Ph, naph; R', R'' = iPr, iPr; **129:** R = Me, D = CH₂=PPh₃
115: R¹, R², R³ = Ph, Ph, Ph; R', R'' = Me, Me; **130:** R = Me, D = CH₂=PPh₃
116: R¹, R², R³ = Ph, Ph, naph; R', R'' = Me, Me; **131:** R = Me, D = CH₂=PPh₃

Chart 3.8 2-Hydroxyimine ligands **102–116**, and complexes **117–131**.



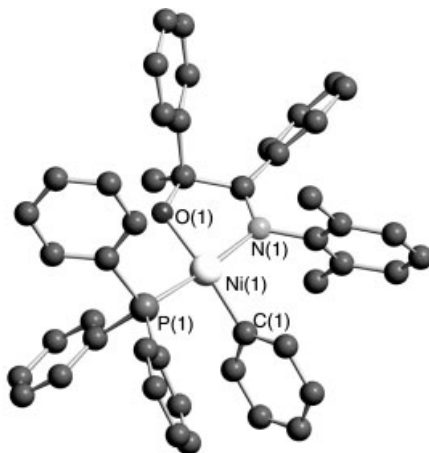
Scheme 3.5 Synthesis of hydroxyimine (N,O)-ligands.

through deprotonation at low temperature, followed by reaction with aromatic ketones or aldehydes. The corresponding hydroxy imines are obtained by a conventional acid-catalyzed condensation with anilines. The latter reaction proceeds satisfactory for sterically less demanding anilines, but not for 2,6-diisopropylphenylamine. However, sterically encumbered hydroxy imines may be obtained through the sequence of aniline condensation reaction with benzil followed by a regioselective nucleophilic addition of an alkyl nucleophile in the form of a Grignard reagent at the remaining keto carbon. High yields are obtained in the nucleophilic addition when Lewis acids such as magnesium dibromide are added as catalyst. Chart 3.8 shows the N,O-ligands that have been synthesized.

Nickel compounds with the hydroxy imine ligands are prepared along two established routes. In the first, *trans*-[NiCl(Ph)(PPh₃)₂] [30] is used as the starting material to yield [N,O]NiPhPPh₃ [14]. With this protocol, complexes **117–125** with ligands **102**, **103**, **105–108**, **109–111** were obtained, respectively. The molecular structure of one example (**123**) is shown in Fig. 3.9. The complex shows a more or less square planar coordination with normal bond distances and a bite angle of 84°. As expected, the five-membered chelate ring yields a more open and accessible coordination sphere than six-membered chelate rings of salicylimine complexes with a bite angle of 95°.

In consecutive screening experiments for polymerization activity (*vide infra*) it was found that the triphenylphosphane donor was not easily removed. Therefore, methyl nickel precatalysts were synthesized starting from (tmeda)NiMe₂ [31] as the nickel reagent, resulting in the formation of several compounds of which (N,O)₂Ni and an oxygen-bridged dimer {(N,O)Ni-Me}₂ were identified by NMR and FAB-mass spectroscopy. However, this mixture of Ni hydroxy imine com-

Fig. 3.9 Molecular structure of (2,6-dimethylphenylimino-2-phenylisopropoxy) NiPh(PPh₃) (**123**). Selected bond lengths (pm): Ni(1)–O(1) = 190.0(6), Ni(1)–C(1) = 191.7(7), Ni(1)–N(1) = 194.4(6), Ni(1)–P(1) = 218.5(4). Selected angles (°): O(1)–Ni(1)–C(1) = 166.6(3), N(1)–Ni(1)–P(1) = 172.4(2), C(1)–Ni(1)–P(1) = 89.8(2), O(1)–Ni(1)–P(1) = 92.1(2), C(1)–Ni(1)–N(1) = 96.0(3).



plexes was inactive in polymerization tests, as was found in other similar cases [8c,d, 32]. Several efforts were undertaken to prepare isolable monomeric (N,O)NiMe(donor) complexes that are useful precatalysts, or could be transformed into such compounds. Nitriles, like acetonitrile or pivalonitrile do not coordinate strongly enough to inhibit dimer formation, and on the other hand phosphanes are not easily removed to afford a vacant coordination site for the incoming monomer (*vide supra*). Nevertheless, in analogy to other (P,O)-Ni polymerization catalysts [8a, 8b], it was found that methylene phosphorane is a suitable donor to prepare the monomeric complexes (N,O)NiMe(donor) (Chart 3.8). By this route, complexes **126–131** were prepared with ligands **104**, **109**, **113–116**, respectively.

In some cases, a second product was also formed in the synthesis. This was identified as a CH activated or ortho-metalated complex (N,O)Ni-(*o*-Ph)PPh₂=CH₂, where an ortho C–H bond of a phosphorane phenyl group was deprotonated by the Ni–Me moiety with concomitant formation of methane. Fig. 3.10 shows the molecular structure of complex **132** obtained from ligand **114**. The central square planar Ni atom is part of two five-membered metallacycles.

It was of importance to establish the formation route of the byproduct, in particular to investigate whether it is a thermal decomposition product of (N,O)-NiMe(CH₂=PPh₃). This is relevant for the polymerization performance because productivity and/or activity are quite sensitive to the thermal stability of the catalytically active species. However, heating (N,O)-NiMe(CH₂=PPh₃) in benzene solution to temperatures well above those employed in polymerization studies did not result in the CH-activation. In fact, the parent nickel methyl phosphorane complexes turned out to be quite stable under those conditions, indicating that the CH-activated product forms during the synthesis along a separate reaction channel. More importantly, it was also established that this byproduct is not polymerization active, nor can it be activated for the polymerization by the procedure used for the (N,O)-NiMe(CH₂=PPh₃) complexes.

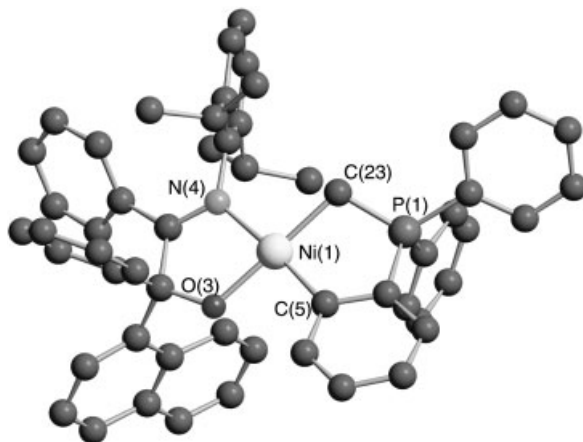


Fig. 3.10 Molecular structure of (2,6-diisopropylphenylimino-2-phenyl-1-phenyl-1-(2-naphthyl)ethoxy) Ni-(*o*-Ph)PPh₂=CH₂ (**132**). Selected bond lengths (pm): Ni(1)–O(3) = 188.02(18), Ni(1)–C(5) = 197.5(3), Ni(1)–N(4) = 197.4(2), Ni(1)–C(23) = 191.4(3),

Ni(1)–sq.pl. = 1.54. Selected angles (°): O(3)–Ni(1)–C(23) = 91.46(9), O(3)–Ni(1)–N(4) = 83.64(8), C(23)–Ni(1)–N(4) = 175.03(10), O(3)–Ni(1)–C(5) = 178.93(10), C(23)–Ni(1)–C(5) = 89.04(11), N(4)–Ni(1)–C(5) = 95.84(10).

3.3

Polymerization Performance

Polymerization of ethene with homogeneous transition metal catalyst in general profits from the addition of a co-catalyst. The usual co-catalysts are aluminum compounds such as MAO, MMAO and/or alkyl aluminum (halides). Their role is that of generating a free coordination site and/or a cationic species as catalyst, and/or to bind trace amounts of catalyst poisons [1–4, 33]. In polymerization with late transition metal compounds a further activation pathway can be used if neutral donors are present [8d, 14] in that activation of the catalyst precursors may be accomplished by addition of reagents that react with the donor, thereby creating a vacant coordination site. Such reagents include Lewis acids such as boranes, (COD)₂Ni, or ammonium or carbonium borates and the like. Here no scavengers for impurities are present, implying that the catalyst should be either robust, or that the reactants are very pure.

In the following sections, the performance of the imine complexes is discussed. It must be noted [11a] that comparing catalyst activity data from different studies is only approximate due to their dependence on experimental conditions, that is reactor geometry, stirring procedure, polymerization time, pressure and the like. Therefore it is advantageous to include known complexes for a direct comparison (“benchmarking”) under identical experimental polymerization conditions. It follows that the catalytic activity and productivity obtained for these known catalysts may differ from the ones reported in the literature; they are characteristic of the equipment and screening procedure used.

3.3.1

Diimine Ni Complexes with Peripheral N-Heteroaromatic Substituents

The general catalytic performance of these metal complexes in polymerization of olefins was screened by the following standard procedure: The complexes (50 or 100 μmol) were activated with 100 mole equivalents of methylalumoxane (MAO) in toluene solution. The polymerization reaction was carried out at a temperature of 30 °C, during which ethene was added with a flow of 40 L h⁻¹. After 4.5 h, the mixture was quenched with methanol, the solid polymer isolated, washed and dried. For benchmarking a nickel diimine complex [12a] with 2,6-(di-isopropyl) phenyl substituents at the imine nitrogen atoms (**133**) was also included. Tab. 3.2 shows the activity and polymer data.

While complexes **31** and **37** show a polymerization activity very similar to **133**, complex **30** exhibits a substantially higher activity. This may be caused by less shielding of the metal center due to less steric bulk of the ligand. This may also account for the much lower molecular weight of the resulting polymer: a more open coordination sphere results in a more competitive chain transfer reaction. The transfer process is thought to be of associative character in olefin, leading to

Tab. 3.2 Polymerizations with nickel diimine complexes^{a)} **30**, **31**, **37**, **133**.

Complex	133	30	31	37
Activity				
(g PE (mmol · h · cat.) ⁻¹)	87.5	122.1	91.3	86.3
M_w^b (g mol ⁻¹)	252,900	9600	208,200	129,000
M_n^b (g mol ⁻¹)	90,400	3250	81,000	19,400
M_w/M_n^b	2.8	3.0	2.6	6.7
Methyl groups ^{c)}				
(CH ₃ /1000C)	76.3	5.2	28.3	70.1
Ethyl groups ^{c)}				
(CH ₃ /1000C)	16.9	0.7	2.8	12.1
Propyl groups ^{c)}				
(CH ₃ /1000C)	7.2	–	1.7	–
Butyl groups ^{c)}				
(CH ₃ /1000C)	7.1	–	2.0	6.0
Pentyl groups ^{c)}				
(CH ₃ /1000C)	4.3	1.5	2.2	4.6
Hexyl and longer ^{c)} groups				
(CH ₃ /1000C)	13.3	8.9	4.0	13.7
Total CH ₃ groups ^{c)}				
(CH ₃ /1000C)	125.1	16.3	41.0	106.5
T_g^d (°C)	–62	n.d.	–29	–62

a) Conditions: 100 equivalents MAO, ethylene 40 L h⁻¹, 30 °C, 4.5 h.

b) Determined by GPC.

c) Determined by NMR.

d) Determined by DSC. n.d.: not determined.

a more crowded 5-coordinate transition state for transfer than a 4-coordinate for insertion [6], 34].

It is interesting to notice that the molecular weight of the polymer produced by complex **31** is quite comparable to the one obtained by **133**, but the branching is different. Complex **31** yields a polyethene with significantly less branching and a substantially higher glass transition temperature (T_g). Both carry the diisopropyl phenyl imine moiety. Obviously, the chain end isomerization and olefin insertion into the secondary nickel alkyl is slower for **31**. Catalysis with complex **37** where one N-hetaryl substituent is the parent phenyl group yields a higher branched polyethylene very similar to **133**, but with half the molecular weight. This shows clearly that the properties of the polyolefin production can be tailored with the ligand frame of the catalyst.

3.3.2

Diiminepyridine Iron and Cobalt Complexes with Peripheral N-Heteroaromatic Substituents

The same general polymerization set up as described for the diimine complexes was used here. The polymerization time was reduced to one hour. In cases that no solid polymer was formed, the organic layer was evaporated to yield an oily residue. Tab. 3.3 summarizes the polymerization results together with relevant properties of the polymers.

From these data, the following general trends can be deduced.

- (i) All the precatalysts **53–62a** containing N-pyrrolyl, -indolyl, -carbazolyl substituents showed remarkably high activities, similar to those of alkyl N-aryl substituted catalysts [13].
- (ii) Iron(II) catalysts **53a–62a** are in general more active by a factor of 10–100 in comparison to cobalt(II) complexes **53b–61b**. The low activity of iron(III) complexes **54c**, **55c** suggests that only Fe(II) and not Fe(III) species are active in catalysis.
- (iii) Increasing the steric bulk of the peripheral N-azolyl groups leads to polymers with higher molecular weight, and a decrease in activity. The highest activity for the homopolymerization of ethene is shown by the 2,5-dimethylpyrrolyl complex **54a**. It is interesting to note that also in the case of alkyl N-aryl catalysts the analogous 2,4,6-trimethylphenyl Fe(II) complex is the most active complex [12–15]. In the cobalt series the most productive complex is **57b** with 2-methyl-5-phenyl-pyrrolyl substituents.
- (iv) The molecular weights of the polymers obtained are in general lower than those of the polymers derived from alkyl N-aryl catalysts [12, 13] but the polydispersities are smaller. The cobalt complexes yield mainly oils of low molecular weight, one extreme case is complex **61b** which yields highly branched oligomers with a chains of less than eighteen carbons (GC analysis).
- (v) Oligomers produced with the N-pyrrole-derived complexes differ substantially from the oligomers obtained from the N-aryl-based systems. While the latter

Tab. 3.3 Results of polymerizations with Fe and Co diiminepyridine complexes.^{a)}

<i>Precatalyst</i>	<i>Amt of Fe/Co [μmol]</i>	<i>Amt of polymer^{b)}[g]</i>	<i>Activity [g polymer/ (mmol Fe/Co)h]</i>			
Iron catalysts						
53 a	50	trace				
54 a	100	56.5	565			
54 c	50	1.0	20			
55 a	100	19	190			
55 c	50	trace				
56 a	50	4	80			
57 a	50	3.6	72			
58 a	50	1.5	30			
59 a	50	3.3 (oil)	66			
60 a	50	16	320			
61 a	50	16 (oil)	320			
62 a	50	0.5	10			
Cobalt catalysts						
53 b	50	trace				
54 b	100	1	10			
55 b	100	5	50			
56 b	50	8.6	172			
57 b	50	11.2 (oil)	224			
58 b	50	0.6 (oil)	12			
60 b	50	0.2	4			
61 b	50	2 (oil)	40			
Polymer properties ^{a)}						
<i>Precatalyst</i>	<i>η^{c)} [dL g⁻¹]</i>	<i>T_M^{d)} [°C]</i>	<i>M_w^{e)}</i>	<i>M_n^{e)}</i>	<i>M_w/M_n^{e)}</i>	<i>Density [g cm⁻³]</i>
Iron catalysts						
54 a	0.1	118	3 401	1273	2.7	0.9241
54 c	0.1	117	2 281	847	2.7	
55 a	1.6	131	112 907	6483	17.4	0.9600
56 a	0.44	120	14 084	1158	12.2	0.9177
57 a	0.22	121	5 438	1320	4.1	0.9338
58 a	0.31	123	8 183	1329	6.2	0.9387
60 a	0.06	63	1 509	727	2.1	0.8913
61 a	0.11	76	1 762	903	2.0	
Cobalt catalysts						
54 b	0.1	118	3 582	1000	3.6	0.9271
55 b	0.45	127	13 600	3181	4.3	0.9605
56 b	0.27	124	4 985	1949	2.6	0.9563
60 b	0.13	120	5 896	1478	4.0	0.9333

a) Conditions: 100 equivalents MAO, ethylene 40 L h⁻¹, 30 °C, 1 h.

b) Yield of oils refer to isolated yields.

c) Viscosity, determined in decalin at 180 °C.

d) Determined by DSC.

e) Determined by SEC.

Tab. 3.4 Types of branching (methyl endgroups/1000C).

<i>Precatalyst</i>	Σ <i>Methyl branches</i>	Σ <i>Ethyl branches</i>	Σ <i>Butyl branches</i>	$\Sigma \geq C_6$ <i>branches</i>	<i>Total methyl branches</i>
61a	19	71	11	80	181
Double bonds (mol%)					
<i>Precatalyst</i>	<i>Vinyl</i>	<i>Vinylidene</i>	<i>Cis/trans</i>	$-CH=C<$	
61a	1.1	0.2	4.3	0.6	

catalysts yield strictly linear oligomers [3d] here a significant degree of branching is observed. The polymer obtained is a complex mixture of different, low molecular weight oligomers. As shown in Tab. 3.4 the amount of double bonds, especially the internal double bonds, is remarkable. Obviously, no single termination pathway is responsible for the formation of the polymers.

From the results discussed above one might speculate on the pathways accessible for the oligomerization and polymerization reaction of ethene. As in the initial studies with late transition metal catalysts [8, 11], there is a delicate balance between insertion of the monomer resulting in a linear polyethene and β -hydride elimination and re-addition, resulting in branching and olefinic products. The branched polyethene produced by catalysts **53a–62** suggests that the latter process, “chain-walking”, is quite important. This is in marked contrast to Brookhart’s and Gibson’s bis(imino)pyridyl Fe and Co complexes which produce highly linear PE, [12, 13], but more like the 1,2-diimine Ni and Pd complexes which yield mainly branched polymers [11]. We can only offer a description of this behavior of catalysts **53a–62b**; it is interesting to note that in essence electronic modification of the peripheral substituents (N-azolyl versus N-phenyl) has such a dramatic effect on the microstructure and physical properties of the polymers.

Polymerization of Propylene The active complex **54a** served as the test case for the polymerization of propylene. Under similar experimental conditions as described above (with propylene as monomer) 15 g of an oily polymer was obtained, corresponding to an activity of 300 g PP/mmol Fe · h. The ^{13}C -NMR spectrum of the polymer shows its atactic nature. In addition, a variety of saturated and unsaturated end-groups could be observed, indicating that again several termination pathways are accessible.

3.3.3

Diimine Palladium and Imine Pyridine Iron Complexes with Halogenophenyl Imine Ligands

Palladium catalysts with diimine ligands based on 2,6-diisopropyl aniline polymerize ethene to a rubbery, highly branched polyethene with low glass transition temperatures [12a]. The interest in these materials results from their possible application as a rubber modifier in engineering plastics [3j,k]. However, the activity of the palladium catalysts is not satisfactory for technical use in a world scale plant. We intended to improve the activity by increasing the Lewis acidity of the metal center by using relatively electron-deficient bromo phenyl diimine ligands.

Polymerization was performed in a 1 L autoclave at 50 °C for 2 h at 6 bar ethene pressure. The N,N-PdMeCl complexes were activated through reaction with one equivalent of sodium hexafluorophosphate. Polymerization results are summarized in Tab. 3.5. It was found that the activity of the bromo derivative indeed is higher, but only by a factor of two. In addition, the molecular weight of the products is lower and the number of branches are higher.

This yields products with extremely low glass temperatures. An evaluation of the distribution of the branches indicates that in the polymerization of ethene with the 2,3-bis(2,6-dibromophenylimine)butane palladium catalyst the ratio of chain walking and subsequent insertion into the secondary palladium alkyl bond is higher and olefin elimination and reinsertion is faster than in the diisopropyl ligand-substituted palladium catalyst (Tab. 3.6). The latter thus results in the production of 1-olefins which – after inserting – give more even numbered branches. The fewer propyl but more methyl branches indicate that isomerization and subsequent ethene insertion is faster than further chain walking. The decreased electron density and somewhat smaller ortho substituents on the phenyl substituents

Tab. 3.5 Pd-diimine complexes

Catalyst (iminesub.)	Activity kg polymer [mol h⁻¹ bar⁻¹]	M_n [kg mol⁻¹]	T_g [°C]	Σ Branches
Br,Br 40	2.1	5	–91	142
iPr,iPr	1.1	35	–65	121

At 50 °C, 120 min polymerization time and 6 bar ethene pressure.

Tab. 3.6 Branching in polyethene from 2,3-bis(2,6-dibromo- and -diisopropylphenylimine)butane palladium methyl chloride/AgPF₆.

Catalyst	Me	Et	Pr	Bu	C₆+
Br,Br 40	39	33	7	16	39
iPr, iPr	36	22	13	12	34

Tab. 3.7 Ethene polymerization with iron diimine pyridine/MAO 66–69

Catalyst (imine sub)	T_{pol} [°C]	Time [min]	Activity tons polymer [mol h ⁻¹ bar ⁻¹]	M_n [g mol ⁻¹]	PDI	T_m [°C]	H_m [J g ⁻¹]
Cl,Cl 66	50–55	15	140	2800	3.0	130	245
Me,Me 68	50–60	15	110	3400	7.8		
Br,Br 67	50	15	6			125	260
iPr,iPr 69	50	20	18				

Polymerization in toluene, 2 bar ethene pressure, MAO co-catalyst, ratio Al/Fe=23 100. PDI: polydispersity index M_w/M_n .

thus give in every aspect a more active catalyst. However, it does not mean a major improvement with respect to a technical process.

The effects of introducing halogens in the 2 and 6 position of phenyl imine catalysts was also studied in diimine pyridine iron dichloride/MAO systems [13]. These catalysts afford linear products with a low olefin content, generally less than one (olefin) functionality per chain. The latter is due to a fast transfer of iron bound alkyl groups to the aluminum compounds that are present in excess. After hydrolysis, alkanes are obtained. When a high ratio of aluminum alkyl to iron catalyst is used, polyethene waxes are obtained due to the statistically favored alkyl group exchange between the metal species.

In Tab. 3.7 the results of polymerizing ethene with various bis(2,6-substituted phenyl imine) derivatives of 2,6-diacetylpyridine are reported.

Polymerization was carried out at a pressure of 2 bar ethene in a 1 L autoclave. The most active derivative with an activity of over 100 tons of polyethene wax per mol iron catalyst carries chloro substituents (Fig. 3.11). In fact this catalyst is so active that the temperature of the solution polymerization reaction could no longer be controlled, even when using extremely small amounts of catalyst. The activity is again higher than the sterically related methyl-substituted system. Also the polydispersity of the product is smaller, probably due to a more dynamic exchange between aluminum and iron (*vide infra*).

In contrast, the bromo derivative readily deactivates under polymerization conditions and has therefore a relatively low (but in absolute number still a very high) activity. The polymers obtained with the catalyst with the halogen containing ligands differ somewhat in crystallinity and/or melting temperature. This is probably due to shorter polymer chains in the case of the bromo derivative. Analysis by ¹³C NMR spectroscopy shows that the waxes are linear within the detection limit of branching.

Several experiments were performed with the 2,6-dichlorophenyl catalyst to obtain insight into the polymerization behavior as a function of the Al/Fe ratio [13b]. Experiments were run in a glass vessel at 1 bar ethene pressure. During polymerization, aliquots were removed, precipitated in methanol, and the isolated polymer was weighted and analyzed (Tab. 3.8).

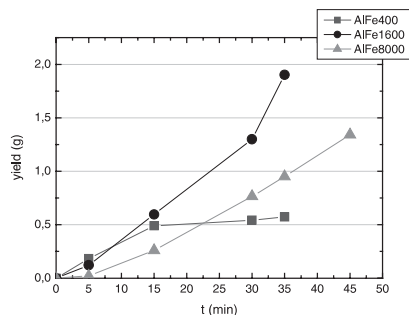
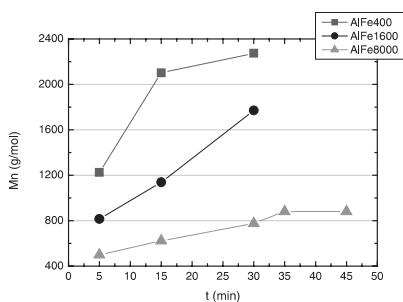
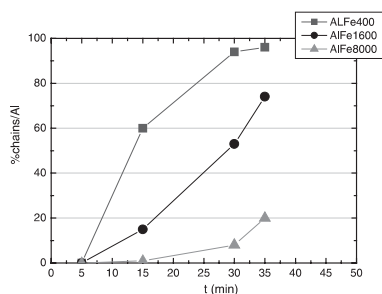
A: Polymer in aliquot**B: Molecular weight****C: Chains/Aluminum**

Fig. 3.11 Ethene polymerization with bis[(2,6-dichlorophenyl)imine]-2,6-diacetamine iron dichloride and various concentrations of MAO. (A): yield, (B): molecular weight M_n , (C): chains/aluminum.

The polymer yield in early stages is higher with a lower ratio Al/Fe. This indicates that alkyl exchange between iron and aluminum is more rapid than ethene insertion into the iron carbon bond. This results in very short chains on aluminum that do not precipitate in methanol. This follows also from the molecular weight of the polymers obtained with various ratios of Al/Fe in time (Fig. 3.12): the higher the ratio, the lower the molecular weight. With a ratio of Al/Fe of 8000, the chain length of the polymer increases linearly with time.

Another effect is obvious from experiments with a Al/Fe ratio of 400: as soon as all the aluminum centers carry one longer hydrocarbon chain, further ethene polymerization proceeds only sluggishly. This indicates the formation of an active catalyst complex between MAO – methyl-substituted aluminoxane – and diimine pyridine iron; with the formed larger alkyl-substituted aluminoxane, such an associate between catalyst and co-catalyst cannot form so readily or is less accessible and the activity is much lower.

In addition, the degree of saturation of the polyolefin increases with the ratio of Al/Fe (Fig. 3.12) depending on the reaction time: with increasing conversion and hence decreasing number of methyl groups on aluminum, the formation of olefins increases. This shows that olefin elimination from an iron alkyl species is

Tab. 3.8 Polymerization of ethene with diimine pyridine iron dichloride (**66**)/MAO.

Entry	Al/Fe	t [min]	Yield [mg]	T _m [°C]	M _n [g mol ⁻¹]	PDI	Sat%
1	400	5	180		1225	2.21	
2	400	15	490		2100	3.78	72
3	400	30	540	100/131	2275	3.92	
4	400	45	1150				
5	1600	5	120	109	815	1.28	
6	1600	15	600	101/122	1140	2.05	89
7	1600	30	1300	101/129	1770	3.37	
8	1600	45	3800	100/129			
9	8000	5	22		500	1.24	
10	8000	15	260		625	1.22	97
11	8000	30	760	97	775	1.28	96
12	8000	45	2680		881	4.73	94

Experiments in toluene (50 mL) at 45 °C, 2 mg (**66**), 1 bar ethene. Sat%: percentage of saturated chains.

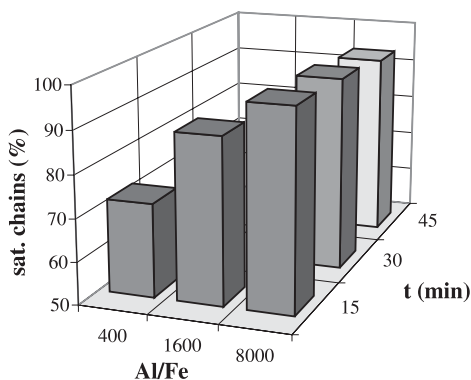


Fig. 3.12 Saturation of the polyolefins as function of Al/Fe ratio and reaction time.

much slower than transfer to aluminum, suggesting that two different catalytic (iron) species are present, one of which has a close interaction with methyl-aluminum [13 h] groups and from which olefin elimination is slow, while the other is a conventional single site catalyst. The degree of unsaturation increases with ethene pressure, thus presumably the olefin extrusion is an associative process as was found for other nickel and palladium diimine catalysts [12].

3.3.4

Salicylimine Ni Complexes

Polymerizations with nickel salicylaldimine complexes **87–101** were performed in a 1 L steel autoclave at 40 bar and 30 °C. The nickel complexes (0.09 mmol) were activated with equimolar amounts of Ni(COD)₂ in toluene solutions for 30 min after which the autoclave was pressurized with ethene. The reaction was terminated after 1.5 h by venting the ethene and the formed polymer powder was isolated. Details are summarized in Tab. 3.9. For comparison, complex **134**, a nickel salicylaldimine complex with a 2,6-(diisopropyl)phenyl imine substituent, was screened under the same conditions.

Nearly all complexes with an unsubstituted phenyl group in the ligand back bone (**87**, **91**, **92**, **134**) show a rather poor polymerization activity. The activity was significantly higher with complexes (**95**, **96**, **99**, **100**) where the phenyl group bears two *tert*-butyl substituents. In addition, the polymers obtained with the latter have a narrow molecular weight distribution while the former display a broad distribution or a low molecular weight. No clear trend arises from the data regarding a structure-activity relationship. In marked contrast to the diimine catalyst systems described above, structural changes in the ligand backbone of nickel salicylaldimine complexes did not impact the polymerization behavior to a major extent.

3.3.5

Hydroxyimine Ni Complexes

The 2-hydroxyimine nickel system was screened for polymerization activity in a six-chamber autoclave (Fig. 3.13) operated at 15 bar and using toluene as solvent. It was found that both types of complexes – NiPh(PPh₃) and NiMe(ylid) – were polymerization inactive and needed a coreagent.

Tab. 3.9 Polymerizations with Ni salicylaldimine complexes.

<i>Catalyst</i>	<i>Activity [gPE [(mmol · h · cat.)⁻¹]</i>	<i>η^{a)} [dL g⁻¹]</i>	<i>M_w^{b)} [g mol⁻¹]</i>	<i>M_n^{b)} [g mol⁻¹]</i>	<i>M_w/M_n^{b)}</i>	<i>Total CH₃^{c)} [CH₃/1000C]</i>
87	96.5	2.27	275,400	12,700	21.6	29.0
91	31.6	0.38	n.d.	n.d.	n.d.	40.6
92	7.3	1.50	102,900	3,900	26.4	34.5
95	125.0	0.57	14,400	8,000	1.8	39.7
96	272.0	0.97	33,200	10,900	3.0	26.1
99	138.2	0.38	12,700	6,900	1.9	35.0
100	287.4	0.10	n.d.	n.d.	n.d.	82.0
134	5.4	0.47	n.d.	n.d.	n.d.	23.7

a) Viscosity, determined in decalin at 180 °C.

b) Determined by GPC.

c) Determined by IR. n.d.: not determined.

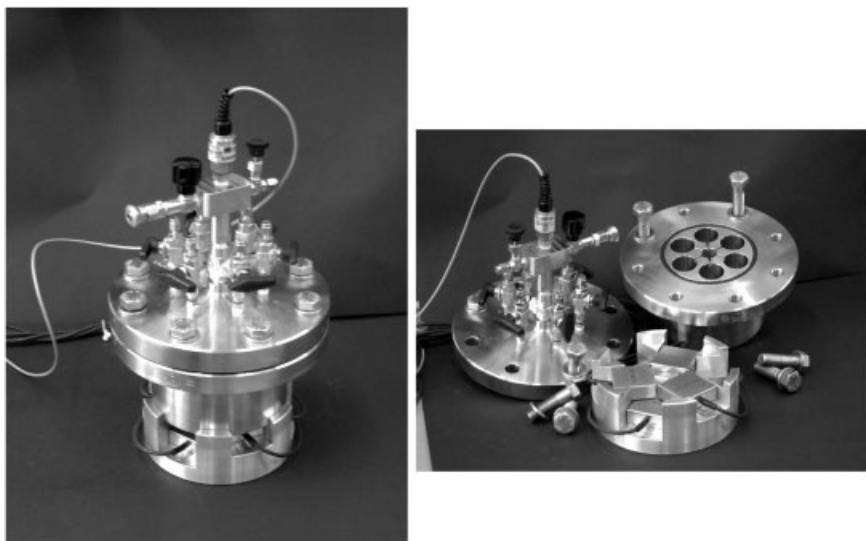


Fig. 3.13 Six chamber autoclave for parallel screening of polymerization catalysts.

The (N,O)-NiR(donor) complexes could effectively be activated by reaction with the triphenylmethylium tetrakis(pentafluorophenyl)borate. With other reagents such as $(\text{COD})_2\text{Ni}$, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate or MAO only traces of polymer were obtained. With tris(pentafluorophenyl)borane an activity below $50 \text{ g PE (g Ni} \cdot \text{h)}^{-1}$ was observed (experiments in toluene at 20°C , 20 bar ethene 5 h).

In Tab. 3.10 data of the initial screening experiments with triphenylmethylium tetrakis(pentafluorophenyl)borate as activator are collected. A more accurate study was performed with the most promising derivatives for ethene polymerization (Tab. 3.11).

The majority of these are (N,O)NiMe($\text{CH}_2=\text{PPh}_3$) compounds. For benchmarking, a recently reported catalyst based on salicylimine (with 2,6-diisopropyl and *o*-5-antracyl substituent) was included in the study (135) [14a]. It can be concluded from Tab. 3.11 that the five-membered alkoxyimine nickel compounds are active catalysts in the polymerization of ethene with activities that compare well with the salicyl imine single site (N,O) nickel catalysts [14]. The activity depends on the substitution pattern of the ligand; highest activities are obtained from complexes that have isopropyl substituents in the ortho positions of the imine phenyl group and two aryl or methyl groups on the alkoxy carbon. Most non-metallocene late transition metal polymerization catalysts contain peripheral 2,6-diisopropylphenyl imine moieties (*vide infra*), therefore it is interesting to see that in this system derivatives with methyl groups at the phenyl group are also fairly active. It might be inferred that, for polymer formation, a minimum steric bulk is a prerequisite, but not necessarily arising from an imine moiety. Fig. 3.14 shows a graphical repre-

Tab. 3.10. Initial screening with hydroxyimine nickel compounds.

Ligand	R^1	R^2, R^3	R', R''	Ni-R R=	Complex	Observation
102	Ph	Me, Me	Me, Me	Ph	117	trace
103	Ph	Me, Me	Me, Et	Ph	118	trace
104	Ph	Me, Me	iPr, iPr	Me	126	polymer
105	Ph	Ph, H	H, H	Ph	119	oligomer
106	Ph	Ph, H	Me, Me	Ph	120	oligomer
107	Ph	Ph, H	Me, Et	Ph	121	oligomer
108	Ph	Ph, Me	H, H	Ph	122	oligomer
109	Ph	Ph, Me	Me, Me	Me	127	polymer
109	Ph	Ph, Me	Me, Me	Ph	123	polymer
110	<i>m</i> -tol	<i>m</i> -tol, Me	Me, Me	Ph	124	–
111	Ph	Ph, Me	iPr, iPr	Ph	125	trace
112	Ph	Ph, iPr	Me, Me			
113	Ph	Ph, Ph	iPr, iPr	Me	128	polymer
114	Ph	Ph, naph	iPr, iPr	Me	129	polymer
115	Ph	Ph, Ph	Me, Me	Me	130	polymer
116	Ph	Ph, naph	Me, Me	Me	131	polymer

Experiments in toluene at 20 °C at 15 bar ethene pressure and 60 min polymerization time, activation with excess tritylborate.

Tab. 3.11 Polymerization data of hydroxyimine nickel compounds.

Compound	R^2, R^3	R', R''	Activity in g pol [g Ni h] ⁻¹	Side chains/1000 carbon atoms	
				Total	Methyl
126	Me, Me	iPr, iPr	1000	5	5
127	Ph, Me	Me, Me	3350	21	10
130	Ph, Ph	Me, Me	800	–	–
131	Ph, naph	Me, Me	1050	–	–
129	Ph, naph	iPr, iPr	3400	9	6
128	Ph, Ph	iPr, iPr	5050	8	6
123	Ph, Me	Me, Me	1000	21	15
135		iPr, iPr	5000	4	4

Experiments in toluene at 20 °C at 15 bar ethene pressure and 60 min polymerization time, stoichiometric activation with triphenylmethylenium tetrakis(pentafluorophenyl)borate.

sentation of the dependence of the activity on the steric bulk of the substituents (z-axis: activity, x-axis: imine substituent, y-axis: alkoxy carbon substituent): Complexes that carry secondary alkoxy instead of tertiary ligands and thus have less bulky coordination sphere tend to give oligomers rather than polymers. Fig. 3.14B is tentatively suggestive of a structure-activity relationship: a certain amount of steric pressure is necessary to achieve polymerization, otherwise oligomers are obtained.

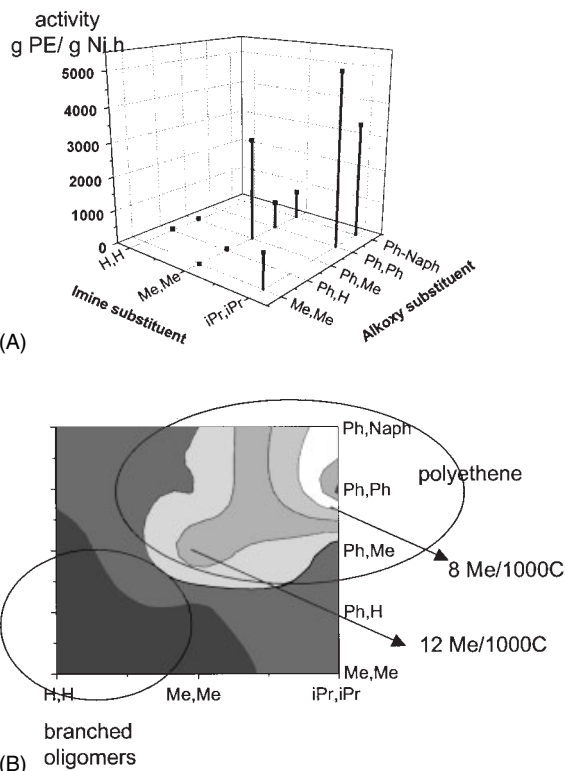


Fig. 3.14 Graphical representation of ethene polymerization with 2-hydroxyimine nickel compounds. Stick plot (A) and corresponding

matrix projection in the x - y -plane (B: lighter shading means higher activity).

The oligomers are a mixture of isomers of $(C_2H_4)_x$ with $x=2-7$ (straight and branched chains with internal and terminal olefins). The polyethene obtained with the 2-alkoxyimine ethane nickel methyl complexes is almost linear. The side chains are generally methyl entities. This is common for nickel based catalysts, where chain running and subsequent ethene insertion into a secondary alkyl group is slow relative to insertion into the primary nickel alkyl species. The catalysts with the highest activity also show the lowest number of side chains. These two observations indicate that in these systems chain walking is rather slow relative to propagation. The occurrence of side chains in the polymer is clearly dependent on the ligand structure of the catalyst. The highest number of side chains is found for the ligand with 2,6-dimethylphenyl imine groups (>12 Me/1000 C). With 2,6 diisopropyl derivatives, approximately 6 methyl groups per 1000 carbon atoms are obtained.

3.4

Concluding Remarks

We have shown that a wide variety of ligand systems with different unusual imine ligands coordinated to iron, cobalt, nickel or palladium give active polymerization catalysts. The synthesis of the ligands is fairly simple, modular and starts from readily available materials, allowing the preparation of whole families of precatalysts by the same synthetic protocol. Highly active catalysts for the polymerization of ethene resulted, and definite differences to “usual” imine precatalysts are observed. The structure–activity relationships that begin to emerge from the catalytic performance of an increasing number of catalytic active complexes will hopefully simplify the future development and/or improvement of polymerization systems.

3.5

Acknowledgements

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3.6

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4

Cycloaliphatic Polymers via Late Transition Metal Catalysis

BRIAN L. GOODALL

4.1

Introduction

Over the past forty years, there have been several reports in the literature regarding the addition polymerization of monocyclic olefins such as cyclobutene [1] and cyclopentene [2] or bicyclic olefins such as norbornene [3] using catalysts related to the original Ziegler-Natta inventions. More recently, interest in norbornene and its derivatives (illustrated in Fig. 4.1) has undergone a renaissance of sorts. This is due to two factors: the development of new single-site catalysts that will polymerize these types of monomers with good activity, and the realization that polymers containing significant quantities of these bicyclic monomers exhibit unique properties such as high glass transition temperatures and transparency.

Early work at Mitsui Petrochemicals concentrated on copolymerization of the multicyclic olefin dimethano-octahydronaphthalene (DMON, structure **II** ($R_1=R_2=H$) in Fig. 4.1), using soluble vanadium catalysts [4] that eventually led to the commercialization of ApelTM polyolefins [5]. Later, the utility of metallocene catalysts for cyclic olefin copolymerization was recognized by both Mitsui and Hoechst [6]. This led to the joint development of the TopasTM line of polyolefins [7], now being marketed by Ticona.

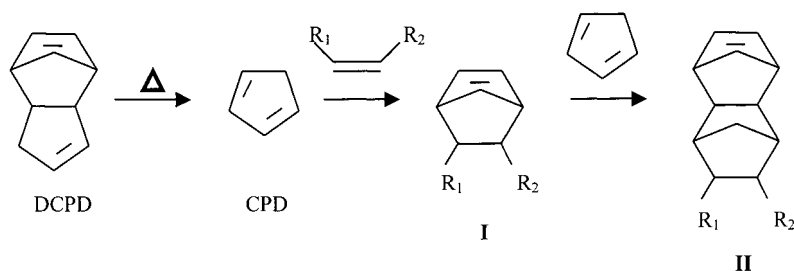


Fig. 4.1 Norbornene monomer synthesis.

This review will attempt to cover all of these polymer types, in particular with reference to developments involving late transition metals. However, there will be a major emphasis on norbornene polymers for a variety of reasons:

- Norbornene monomers can be (co-)polymerized by a variety of polymerization pathways, offering significant diversity.
- Norbornenes represent a wide variety of monomers and hence polymers and application areas.
- This area is developing into a number of possible commercial applications, thanks in part to some pioneering work carried out at my old group at the B.F. Goodrich Company, as well as a number of other companies using both early and late transition metal catalysts.

There are three different mechanisms by which the cyclic olefin norbornene can be polymerized to reasonably high molecular weights: ring-opening metathesis polymerization (or ROMP), vinyl addition copolymerization with acyclic olefins such as ethylene, and vinyl addition homopolymerization (see Fig. 4.2). Carbocationic and free-radical initiated polymerizations are ignored since they yield only low molecular weight oligomers [8].

The polymerization of strained cyclic olefin monomers, such as norbornene, finds its roots in the 1950s with the work of Andersen and Merckling [9] who were the first to report ROMP polynorbornene. Since then, olefins such as cyclopentene, cyclooctene, and norbornene have been used, with varying degrees of commercial success, as constituents in elastomeric materials (i.e., those with relatively low glass transition temperature, T_g). In this regard ROMP materials such as Vestenamer® (polycyclooctene) and Norsorex® (polynorbornene) come to mind. None of these polymers are cycloaliphatic since they are all highly unsaturated, and the polymers derived from mono-cyclic olefins are linear in nature. The polymers resulting from bicyclic and polycyclic olefins (e.g. norbornene and its higher homologs) afford truly cycloaliphatic polymers only after hydrogenation.

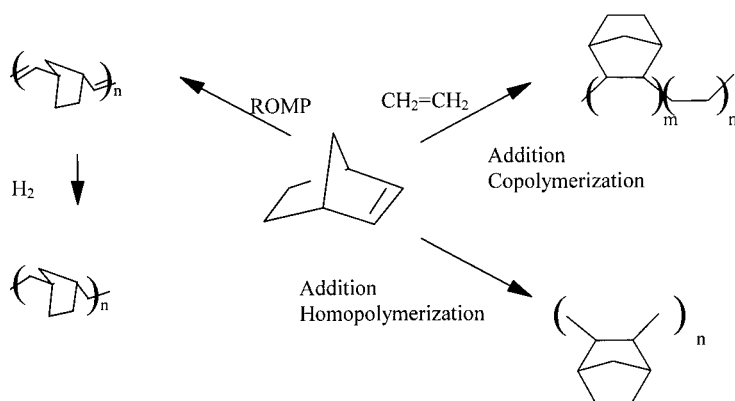


Fig. 4.2 Norbornene polymerization pathways.

For these reasons relatively little attention is given to ROMP technology in this review.

B. F. Goodrich commercialized a ROMP thermoset material known as Telene[®], a liquid reaction molding resin based on the reaction injection molding (RIM) of norbornene-type monomers such as dicyclopentadiene (DCPD). The high degree of multicyclic monomers in this formulation imparts a high T_g to the material (typically about 150 °C). This RIM system takes advantage of B. F. Goodrich proprietary catalyst and co-catalyst technology [10] to provide a material that has a unique combination of stiffness and toughness. The catalyst systems consist of two components, one component being dissolved in each of two liquid monomer streams (mainly DCPD) which are mixed in a mold to give rise to the final composition. The pro-catalyst comprises a long-chain alkylammonium molybdate (the alkyl chains impart solubility, while the molybdate supplies molybdenum in a non-Lewis acidic form, preventing carbocationic gelation of the monomer mixture) and the co-catalyst is typically an ethylaluminum halide species modified (for example with an alkoxy group) to induce an induction period permitting the mold to be filled prior to the onset of the exothermic ROMP reaction that gives rise to the final thermoset part. Telene liquid reaction molding resins and parts are now manufactured and distributed by Cymetech. Under license to Goodrich, Nippon Zeon commercialized a similar product in Japan, using similar catalyst technology, under the name Pentam[®]. Virtually simultaneously Hercules launched a similar product named Metton[®]. The Hercules catalyst technology also applies two component catalysts, a hindered phenoxytungsten halide pro-catalyst and a diethylaluminum chloride co-catalyst modified with a Lewis base or similar additive to impart the desired control over the onset of polymerization. The materials are now manufactured and marketed by Metton of America. Patents have appeared in which ruthenium catalysts are applied for the same application [11].

In terms of thermoplastic polymers made using ROMP methods the commercial products can be sub-divided, into two categories, based on the glass transition temperature or melt-processing temperature of the polymer. Early products were elastomers, the low T_g s of which permit processing at low temperatures so that their unsaturated nature presents no major stability problems. Interestingly Goodyear filed early patents [12] describing a RIM process, using ROMP catalysts, to produce automobile tires in a mold using cyclopentene as the monomer (but this novel approach was never commercialized). Although it is possible to obtain higher T_g thermoplastics based on ROMP chemistry depending on the monomer chosen, hydrogenation of the unsaturated backbone is necessary to afford thermooxidative stability to the polymer [13]. Thus hydrogenation is required, primarily to allow the high T_g polymers to be melt-processed. In the case of the high T_g RIM thermoset materials (above) hydrogenation is clearly not an option; however, in the case of RIM oxidation this is not a major problem since the polymer is formed directly as the finished part, and secondly surface oxidation is limited by the relatively impervious nature of the polymer. In fact a little surface oxidation is an advantage since it allows the parts to be directly painted without a separate priming step.

4.2

The Addition Polymerization of Cyclic Olefins

This extensive section deals with the late transition metal-catalyzed homopolymerization of cyclic olefins to afford cycloaliphatic polymers, or saturated polymers in which the cyclic structure of the monomer remains intact in the polymer backbone.

4.2.1

Cyclopropenes and Cyclobutenes

Unsubstituted cyclopropene is thermally unstable and polymerizes spontaneously and uncontrollably at temperatures exceeding -78°C [14]. 3,3-Dialkylcyclopropenes have been shown to undergo controlled addition polymerization using cationic palladium catalysts [15]. The catalysts used were ionic (η^3 -allyl)palladium complexes with chelating N,N-ligands and a hexafluoroantimonate counterion. The ligands reported were 2,2'-bipyridyl, sparteine and C_2 -symmetric bisoxazoline. The polymers had molecular weights (M_n) up to in excess of 50 000, comprised the expected triangular repeat units, and are partially crystalline with moderate thermal stability.

Surprisingly there have been no reports of late transition metal-catalyzed addition polymerization of cyclobutenes. Since the homopolymerization of cyclobutene using metallocene catalysts is exemplified in the literature [16] it is only a matter of time before a report of a cationic palladium or nickel catalyst for the polymerization appears in the literature.

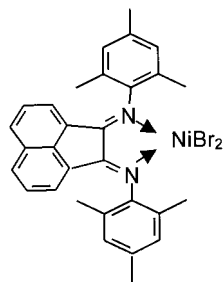
4.2.2

Cyclopentene

Cyclopentene can be polymerized using a variety of metallocene catalysts to afford poly(cyclopentene)s with 1,3-enchainment of the cyclopentane units [17]. These polymers are invariably of low molecular weight ($M_n < 2000$) and often highly isotactic, and are generally not melt-processable [18].

Polymerization of cyclopentene by both cationic nickel and palladium catalysts with hindered di-imine ligands ("Brookhart catalysts") results in the formation of new poly(cyclopentene)s with a different crystalline form [19]. The rates of polymerization are very slow; for example, the nickel catalyst illustrated in Fig. 4.3 in combination with an ethylaluminum dichloride co-catalyst converted 4600 moles of cyclopentene but took a week to do so [20]. The resulting polymer was all-*cis*, exhibited a T_g of 97°C , a melting range of 160 – 285°C and a molecular weight (M_n) of 73 000 with a polydispersity of around 4. Average molecular weights can be as high as 250 000 using these catalysts and the broad melting points are in the range of 240 – 330°C .

Fig. 4.3 Brookhart catalyst for cyclopentene polymerization.



4.2.3

Norbornenes

The addition copolymerization of norbornene-type monomers with α -olefins [21] forms the basis of EPDM (ethylene propylene diene monomer) technology. Incorporation of small amounts of DCPD or ethylidene norbornene (ENB) in olefinic vinyl addition polymers provides latent crosslink sites in EPDM elastomers. It is well known in the literature that incorporation of higher amounts of rigid, bulky multicyclic olefins results in materials with higher T_g s [22]. In fact, more recent work has concentrated on increasing the T_g of norbornene-type monomer/ α -olefin copolymers [23]. The use of late transition metal catalysts to prepare such copolymers is reviewed in Section 4.3.

The vinyl addition homopolymerization of norbornene, resulting in poly(2,3-norbornene) was first mentioned in the early 1960s using classical TiCl_4 -based Ziegler systems [24]. These catalysts afforded only very low molecular weight materials (molecular weights <1000) at low yields. Zirconocene/methaluminoxane systems are reported to afford high polymers, but these polymers decompose in air at high temperatures before they melt and are insoluble in organic solvents [25]. Furthermore, for the homopolymerization of norbornene zirconocene addition catalysts exhibit low activity and require the use of a large excess of expensive methaluminoxane (MAO). Electrophilic palladium(II) complexes effect the “living” polymerization of norbornene [26, 27]. For example, cationic palladium complexes such as $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, in solvents such as nitromethane, were found to homopolymerize norbornene to high polymers with reasonable solubility in solvents such as tetrachloroethylene, chlorobenzene and *o*-dichlorobenzene. These polymers exhibit molecular weights in excess of 100 000 and also were found to have high glass transition temperatures ($T_g > 300^\circ\text{C}$). Three brief reviews of the vinyl polymerization of norbornene have recently appeared [28].

Thus, until the last decade, three families of catalysts have been reported to catalyze the addition, or “vinyl-type” homopolymerization of norbornene resulting in poly(2,3-bicyclo[2.2.1]hept-2-ene). These three catalyst types are the classical TiCl_4 -based Ziegler systems (type 1), the zirconocene/aluminoxane systems (type 2) and certain electrophilic palladium(II) complexes (type 3).

The homopolymerization of norbornene is described in a process patent to Idemitsu Kosan [29]. This patent application describes the use of catalysts compris-

ing Group V–VIII transition metal salts in combination with MAO as co-catalyst. In a way this type of catalyst is a hybrid of all three of the above catalyst families, being a Ziegler catalyst type (type 1), using a large excess of MAO as co-catalyst (type 2) and using Group V–VIII transition metal salts (e.g. palladium) (type 3). Typical Group V–VIII transition metal salts used in this patent include nickel bis(acetylacetonate), bis(cyclopentadienyl)nickel, palladium chloride, chromium bis(acetylacetonate) and manganese bis(acetylacetonate).

Similarly to the zirconocene/MAO catalysts, the activity of the Idemitsu catalyst systems is poor when the whole catalyst system (catalyst+co-catalyst) is taken into account. In the very best example (in terms of catalyst activity and polymer yield) nickel bis(acetylacetonate) was used in combination with MAO (molar ratio 1:200) to homopolymerize norbornene in toluene at 50 °C for 4 h affording a 70% conversion into high molecular weight (M_w 2.2×10^6), toluene-soluble poly-(norbornene). The ratio of norbornene to nickel was 20 000:1 and the ratio of norbornene to aluminum was only 100:1. Thus, while the yield of polymer is high based on the nickel catalyst (25 700 g per g nickel), the yield based on aluminum is very poor (260 g per g aluminum or about 120 g per g MAO). It can readily be estimated that the cost of the MAO activator alone would add significantly to the cost of the polymer, as well as requiring costly removal of catalyst residues from the polymer.

The polymers produced in this patent application could not be melt processed (they were cast from solution) since their glass transition temperature (T_g) is too high and there is no method taught to control the T_g . Furthermore there is no method taught to control polymer molecular weight.

The first significant discovery of my old group at B.F. Goodrich was a broad family of new single component and multi-component catalysts for the vinyl addition polymerization of norbornene-type monomers based on nickel and palladium. Unlike the ROMP route, a saturated (i.e., thermally and oxidatively stable) polymer is generated in a single step, and unlike the ethylene/norbornene copolymerization route it is possible to achieve complete conversion of the norbornene monomer, eliminating the need for recycling of the monomer. Using these catalysts in combination with a novel chain transfer technology, it is possible to control molecular weights from a few hundred to several million, affording novel olefin-terminated polymers. It is also possible to tailor the glass transition temperature (from a high of about 370–390 °C for homopolynorbornene) by copolymerization of selected 5-alkylnorbornenes with norbornene. Furthermore, these new catalysts, especially palladium, have such a high tolerance toward functional groups (such as carboxylic acids and esters) that homo- and copolymerization of a wide variety of norbornene monomers bearing functional groups is possible. These catalyst systems have been disclosed in patents [30] or in preliminary communications [31].

4.2.3.1 Nature and Scope of the Catalyst

A sizeable number of well-defined, single component Group VIII transition metal catalysts were synthesized in our laboratory at B.F. Goodrich. Two of these are illustrated in Fig. 4.4. The most active catalysts of this class are invariably the nickel systems.

These systems were extensively studied with the goal of finding even better, more efficient catalysts. Based on these studies it appears that the key attributes for high activity appear to be three-fold: (1) the transition metal center is complexed only by metal olefin π -bonds and a metal-carbon σ -bond (which can be part of an allylic system), (2) the metal center is cationic, and (3) the counter-ion is a weakly coordinating anion.

Thus, for a highly active, single-component catalyst for the addition polymerization of norbornenes it seems that a necessary requirement is accessibility to the metal by the norbornene substrate. We refer to this family of catalysts as being "naked" since all of their ligands (olefins) are readily displaced by the norbornene monomer to afford a highly active cationic metal nucleus; nickel catalysts being preferred. The envisaged active site is illustrated in Fig. 4.5.

Catalysts of this type have been studied extensively for the polymerization of butadiene [32], the oligomerization of styrene [33], and the dimerization of acrylates [34]. Indeed it was my becoming aware of this work that led to all of our subsequent discoveries.

In late 1992, Professor Lido Porri (Polytechnico di Milano) visited B.F. Goodrich Research and Development Center in Brecksville, Ohio and gave a lecture on the Ziegler-catalyzed polymerization of dienes such as butadiene, and styrene, making comparisons between the two areas of catalysis. In a discussion following that talk he mentioned π -allylnickel complexes and made particular reference to the work of Tkatchenko et al. [35] where a nickel compound had been used to oligomerize styrene to give isotactic oligomers. It occurred to me that these nickel

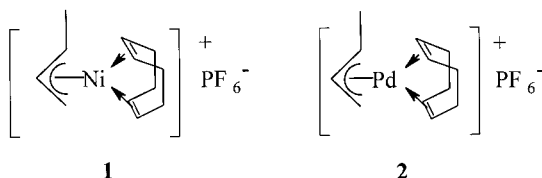


Fig. 4.4 Naked nickel and naked palladium.

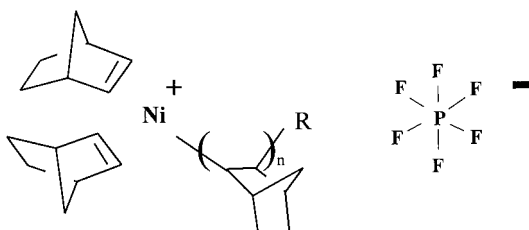


Fig. 4.5 Proposed active site (from naked nickel).

complexes, and in particular the illustrated “naked nickel” catalyst (**1** in Fig. 4.4), by virtue of its unhindered structure, may make excellent catalysts for the polymerization of norbornenes. I reasoned that all of the ligands on the nickel would be readily displaced by norbornene (a relatively strong π -donor) to afford an active polymerizing center (nickel) with a growing polymer chain and ligated only with norbornenes (incoming monomer units). In other words the metal center is “naked” since it bears only the growing polymer chain and incoming monomer units with no shrouding or hindering ligands (Fig. 4.5). We synthesized the compound and it transpired that the new “naked nickel” catalyst is indeed capable of polymerizing norbornene to high conversion. Furthermore we discovered, to our surprise, that the catalyst (even in the absence of any activators) had (at that time, in late 1992) an unprecedented activity in the polymerization of norbornene (in the very first experiment, using methylene chloride as diluent [b.p. 40 °C], the reaction was so rapid and exothermic that it popped the reactor cap within 5 s, spewing polymer with a molecular weight exceeding 2 million over the fume-hood). We achieved *very* high conversions (essentially quantitative) even at norbornene:nickel ratios of 2000:1 at room temperature within less than 30 s.

4.2.3.2 Reaction Injection Molding (RIM) of Norbornenes

The sheer activity of these new nickel norbornene polymerization catalysts and their very rapid polymerization rates makes them potential catalysts for a new norbornene-RIM (reaction injection molding) technology to afford a saturated, oxidatively stable RIM part rather than the unsaturated ROMP (ring-opening metathesis polymerization) polymer that is the current commercial Telene[®] or Metton[®]. Fig. 4.6 illustrates the concept and also exemplifies the very rapid polymerization rates that are observed.

In this particular experiment the naked nickel catalyst was dissolved in a small amount (0.5 mL) of 1,2-dichloroethane and injected into a mixture of norbornene-type monomers (4000 moles per mole nickel). If pure norbornene was used, the reaction ensued so rapidly that it could not be controlled and something resembling a cross between catalyst encapsulation and an explosion occurred. By introducing a norbornene monomer bearing endo-, exo-substituents in the 5-position it proved possible to control the reaction to the point that we observed a gel-time as shown in Fig. 4.6. An added benefit to using alkylnorbornenes as monomers is their lower freezing points (liquid at ambient temperature, unlike norbornene which melts at 34 °C) and higher boiling points (which obviates the problem of boiling monomer during the RIM exotherm).

Fig. 4.6 is included for the purpose of illustrating the “explosive” rate of these polymerizations, while it does also suggest that a new RIM technology may be conceivable based on this new addition-type polymerization. Indeed with further catalyst development (described in the following sections) this concept gave rise to a new in mold polymerization technology with a variety of possible applications, including RIM [36].

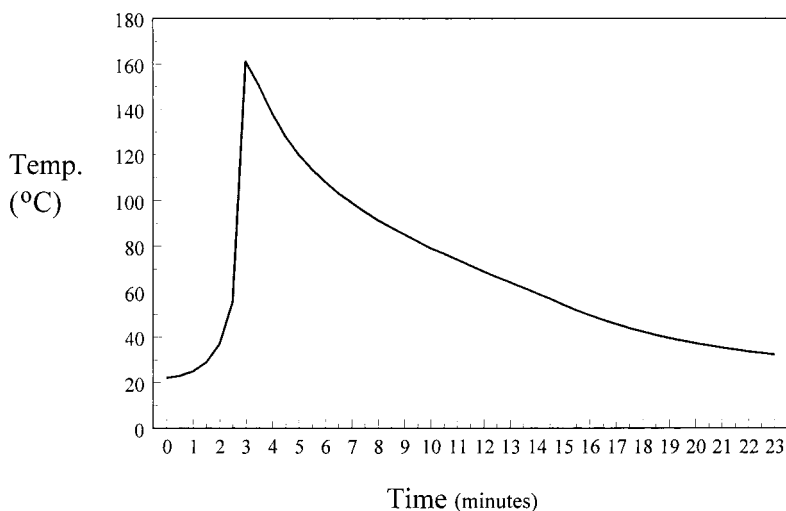


Fig. 4.6 Typical temperature profile of a bulk norbornene polymerization using naked nickel (early RIM experiment).

4.2.3.3 Catalyst Synthesis and Polymerization of Norbornene

Catalyst 1, $[(\eta^3\text{-crotyl})(\text{cycloocta-1,5-diene})\text{nickel}]\text{hexafluorophosphate}$ ("naked nickel"), was prepared following a procedure developed for the methallyl isomer by Tkatchenko and coworkers [35, 37]. Thus bis(cyclo-1,5-octadiene)nickel was reacted with crotyl bromide to yield the bromide-bridged $(\eta^3\text{-crotyl})\text{nickel}$ dimer. Abstraction of the bromide by thallium hexafluorophosphate in the presence of cyclo-1,5-octadiene yielded 1. The structure of 1 in solution is consistent with its solid state X-ray crystal structure [38].

Naked nickel (1) is a very effective catalyst for norbornene polymerization. Addition of 1 to 1,2-dichloroethane solutions of norbornene (norbornene: Ni molar ratio of 2000:1) gave conversions of norbornene homopolymer typically exceeding 95% after about 1 h.

A series of homopolymerizations of norbornene and copolymerizations of norbornene and 5-decylnorbornene were carried out at a 4000:1 monomer to catalyst ratio using catalyst 1. The polymerizations were conducted at room temperature for 1 h before short stopping the reaction. The results of these runs are presented in Tab. 4.1.

The conversions of monomer to polymer were excellent. It should be pointed out that while the reactions were typically run for an hour, it was clear that the monomer was very highly converted within the first couple of minutes (indeed, as mentioned above, the very first reaction resulted in high conversion of 2000 moles of norbornene within 3 s!).

Catalyst 2, $[(\eta^3\text{-crotyl})(\text{cyclo-1,5-octadiene})\text{palladium}]\text{hexafluorophosphate}$ ("naked palladium", Fig. 4.4), was prepared similarly to that of its nickel analog. First the chloride-bridged dimer, $[(\eta^3\text{-crotyl})\text{Pd}(\mu\text{-Cl})]_2$, was synthesized, followed by addition

Tab. 4.1 Polymerization of norbornene and 5-decylnorbornene using catalyst 1 (naked nickel) with and without 1-decene as a chain transfer agent.

Run ^{a)}	Norbornene: 5-decylnorbornene	Decene-1 (mol%)	Conversion (%)	10 ³ M _w	M _w /M _n	T _g
1	99.5:0.5	1	92	195	2.44	353
2	99.5:0.5	1.5	93	124	2.82	351
3	97:3	1.5	90	125	2.31	356
4	85:15	0.5	87	310	2.40	285
5	95:5	2	94	114	2.59	336
6	90:10	1.5	90	128	2.37	297
7	99:1	0.5	96	331	2.83	375
8	85:15	2	92	110	2.20	265
9 ^b	100	25	100	11	1.83	274
10 ^c	100	0	87	1250	3.73	370

a) Runs 1–8 in 1,2-dichloroethane for 1 h at room temperature with a monomer to Ni ratio of 4000:1.

b) Runs 9 and 10 at 2000:1 monomer to Ni ratio.

c) Run 10 for 30 min.

of thallium hexafluorophosphate in the presence of cyclo-1,5-octadiene to yield catalyst 2 [39].

The polymerization of norbornene using catalyst 2 is much more sluggish than with 1. Even after 24 h (albeit at a 4000:1 molar ratio of norbornene to palladium) in 1,2-dichloroethane, only 66% conversion to poly(norbornene) was achieved. The difference in rate observed between nickel and palladium was used to our benefit in determining the initiation event, as explained in the following section.

4.2.3.4 On the Mechanism of Initiation

Once this new family of catalysts was proven to show excellent polymerization activity and versatility (see below) in the polymerization of norbornenes, we immediately set out to understand the mechanism by which the polymerization occurs. The mechanism is of importance not only in the design of other, and possibly better, catalysts but also in helping to establish the microstructure of the polymers formed.

In an attempt to study the initiation event for norbornene polymerization, the following NMR tube study was undertaken. The ¹H NMR spectrum of 1 in CDCl₃ was recorded. Approximately 2–3 equiv of norbornene per nickel were added to this solution and the spectrum was acquired again. No significant change in the catalyst is evident; only signals due to unreacted 1 and norbornene were observed. Within 10 min the spectrum was recorded once again. Broad signals due to poly(norbornene) were observed as well as unreacted 1 and norbornene. These observations are consistent with a slow initiation rate followed by an extremely rapid rate of propagation.

Fig. 4.7 exo-Insertion product of norbornene into catalyst **2** (naked palladium) (numbering system corresponds to Fig. 4.8).

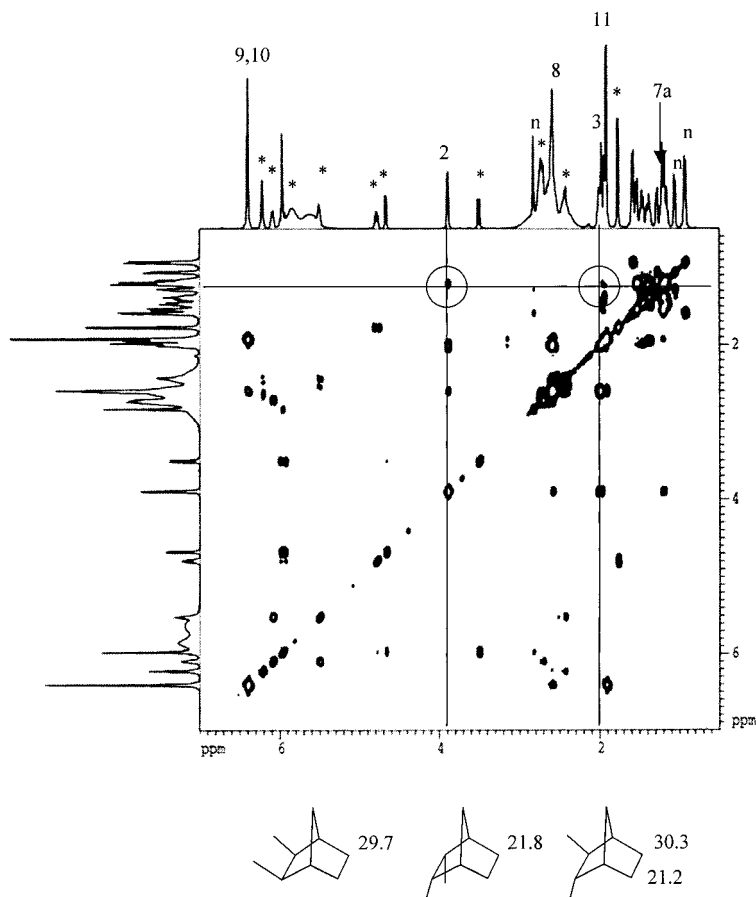
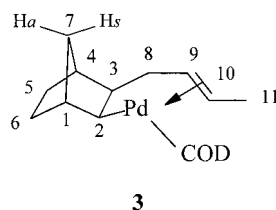


Fig. 4.8 ^1H - ^{13}C 2D correlation spectrum of the reaction mixture of naked palladium (marked * in the spectrum) and norbornene (marked n in the spectrum) and model compounds (numbering system corresponds to Fig. 4.7).

By contrast, when a sample of catalyst **2** was dissolved in CDCl_3 and about 1 equiv of norbornene were added, the resulting reaction was so slow that the insertion reaction could be followed by NMR spectroscopy. After addition of an equivalent of norbornene, the ^1H NMR spectrum was taken within 30 min. Along with

resonances for unreacted **2** and norbornene, there are peaks due to the exo-insertion product of norbornene into the crotyl-Pd bond, complex **3**. The very broad peaks observed for the COD ligand are consistent with a monodentate COD which is undergoing dynamic exchange. Characterization of **3** (Fig. 4.7, numbering scheme corresponds to Fig. 4.8) as the exo-insertion product is in line with previous work by Hughes and Powell [40] in which NMR evidence showed that insertion of strained olefins (norbornene, norbornadiene, etc.) into the Pd-allyl bond of $(\eta^3\text{-allyl})\text{Pd}(\text{Hf}(\text{acac}))$ (Hf(acac)=hexafluoroacetylacetonate) occurred on the exo face. An X-ray crystal structure of the 2-methallyl insertion product with an acetate ligand confirmed this stereochemistry [41].

The structure of complex **3** was elucidated using ^1H 2D-COSY and 2D ^1H - ^{13}C NMR techniques (Fig. 4.8, numbering scheme corresponds to Fig. 4.7). The exo insertion product is confirmed in the 2D-COSY spectrum which exhibits the expected four-bond, long range coupling between the endo protons 2 and 3 and the anti proton 7a in the CH_2 bridge of the norbornene moiety due to a "W" conformation that relates the protons [42]. Further evidence for exo insertion of norbornene in complex **3** comes from its ^{13}C NMR spectrum. In the model compound *exo*-2,3-dimethylnorbornene carbons corresponding to 5 and 6 resonate at 29.7 ppm, whereas for *endo*-2,3-dimethylnorbornane these carbons are shifted upfield to 21.8 ppm. A similar chemical shift pattern is observed in *exo,endo*-2,3-dimethylnorbornane [43]. Thus, the fact that the 2D ^1H - ^{13}C NMR spectrum of complex **3** allows for the assignment of signals at 28.7 and 29.3 ppm to carbons 5 and 6 is consistent with an exo-substitution at carbons 2 and 3.

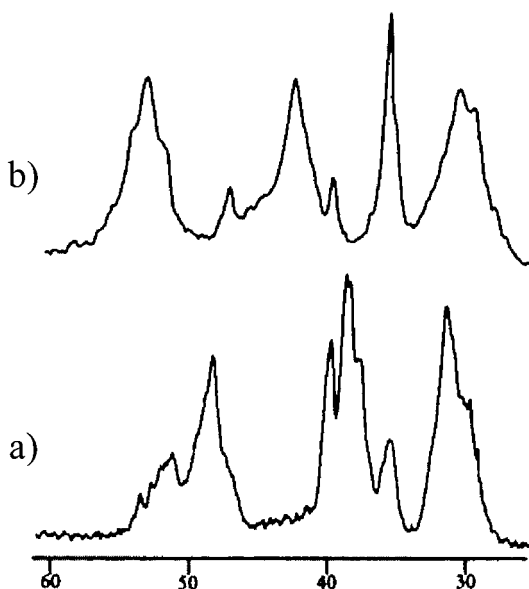
4.2.3.5 Poly(norbornene) Microstructure

The ^{13}C NMR spectra of the poly(norbornene) produced by catalyst **1** (naked nickel) and **2** (naked palladium) are given in Fig. 4.9a and b, respectively. Based on the different NMR signatures of these two polymers, their microstructures are obviously different. However, the absence of resonances upfield of 28 ppm (see 2,3-dimethylnorbornane model compounds above) in either spectrum proves that subsequent monomer insertions occur on the exo face of norbornene. Therefore, any microstructural differences between the poly(norbornene)s must be attributed to differences in tacticity.

The polymers were studied in more detail using ^1H - ^{13}C correlation spectroscopy. The results of these studies are presented in Fig. 4.10a and 4.10b for poly(norbornene) made using catalyst **1** and **2**, respectively.

The spectra of both polymers can be readily separated into methine and methylene regions; those resonances appearing upfield of 40 ppm in the ^{13}C NMR spectrum are due to methylene carbons and those downfield are due to methine carbons. Of special interest are the cross-peaks due to the bridging methylene group C7 (between 36 and 39 ppm, circled in the spectra). As expected, the carbons in this region correlate with the two inequivalent protons H_{7a} and H_{7s} attached to the bridge carbon, C7. However, in the nickel-based polymer, there are two distinct types of bridging carbons, while in the palladium polymer there is only one

Fig. 4.9 (a) ^{13}C NMR spectrum of poly(norbornene) made with naked nickel, (b) ^{13}C NMR spectrum of poly(norbornene) made with naked palladium.



type. This pattern persists in other regions of the 2D spectrum. For the polymer backbone carbons 2 and 3, which appear the farthest downfield in the ^{13}C NMR spectrum, there are two rather strong crosspeaks at about 49.5 and 50.5 ppm in the nickel-based polymer. In the palladium-based polymer only one strong crosspeak appears in this region at around 53 ppm. From this analysis, the palladium polymer microstructure is clearly more regular than the nickel poly(norbornene).

Prior to these studies the first indication of major architectural differences between the nickel- and palladium-catalyzed poly(norbornene)s was in their grossly different solubility behavior. The nickel-based poly(norbornene) is highly soluble in simple hydrocarbons such as heptane and cyclohexane at room temperature even at very high molecular weights ($>1\,000\,000$). Using the palladium catalysts, it was observed that the poly(norbornene)s generated are insoluble in simple hydrocarbons but, at lower molecular weights, can be coaxed into solution using hot *o*-dichlorobenzene. This remarkable difference in solubility characteristics shows that there is clearly a large difference in polymer architecture between the nickel- and palladium-derived polymers, necessitating the isolation and characterization of poly(norbornene) oligomers to fully elucidate the microstructure (see Section 4.2.3.7).

4.2.3.6 On the Mechanism of Propagation and Chain Transfer

In the course of our polymerization studies the performance of these new catalysts in the copolymerization of norbornenes with α -olefins such as ethylene, 1-hexene and 1-decene was investigated. The primary reason for exploring this area was to enable copolymerization of norbornenes with ethylene (and other α -olefins)

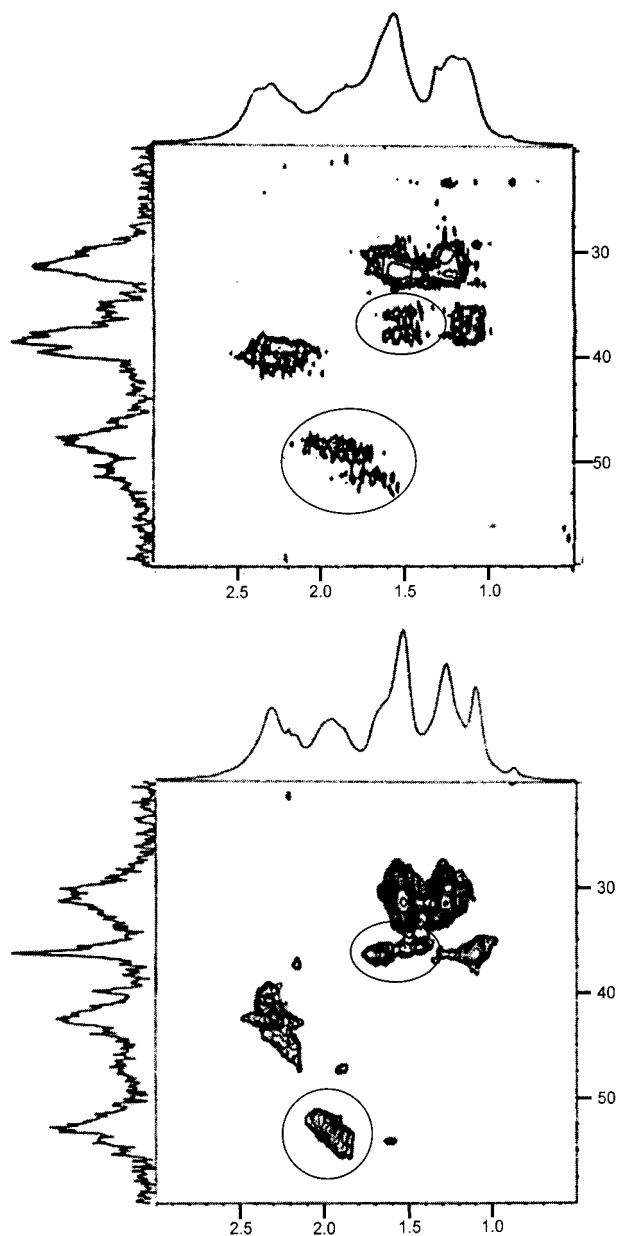


Fig. 4.10 ^1H - ^{13}C Heteronuclear correlation spectra of poly-(norbornene) made with (a) naked nickel and (b) naked palladium.

and hence tailor the high T_g to the range where melt-processing is possible ($<250^\circ\text{C}$). This result was eventually achieved by using appropriate chelate ligands with both nickel and palladium catalysts (Section 4.3).

In the case of “naked nickel”, rather than being incorporated as co-monomers these olefins drastically reduced the molecular weight of the resulting polynorbornene. This dramatic effect on the weight average molecular weight is plotted in Fig. 4.11.

A first glance at Fig. 4.11 suggests that the effect of olefins on polymer MW is catastrophic, since at 30 mol% 1-decene the products are in the trimer-hexamer range ($M_w < 1000$); however, further study revealed that the control of MW is very precise and controllable. Indeed, the addition of controlled levels of 1-decene (or other α -olefins) proved to be a very reproducible way to achieve any desired MW from oligomers up to very high MW polymers. This is illustrated in Fig. 4.12, where it can be seen how precisely the molecular weight can be controlled, and that similar molecular weights result whether the studied polymerization is a homopolymerization of norbornene itself or a copolymerization with alkylnorbornenes.

Using NMR techniques, it was established that a norbornene polymerization carried out in the presence of an α -olefin yields poly(norbornene) with olefinic unsaturation as the polymer end group. This is readily observed for poly(norbornene) samples, particularly for lower molecular weight poly(norbornene), made using ethylene as the chain transfer reagent. The ^1H NMR spectrum of such a low molecular weight polymer is shown in Fig. 4.13. Note that in addition to the expected aliphatic protons between 0.7 and 2.3 ppm, there are signals due to olefinic protons between 4.7 and 5.0 and between 5.6 and 5.9 ppm. The 2:1 relative intensity of these two olefinic groups of signals is consistent with the presence of a vinyl

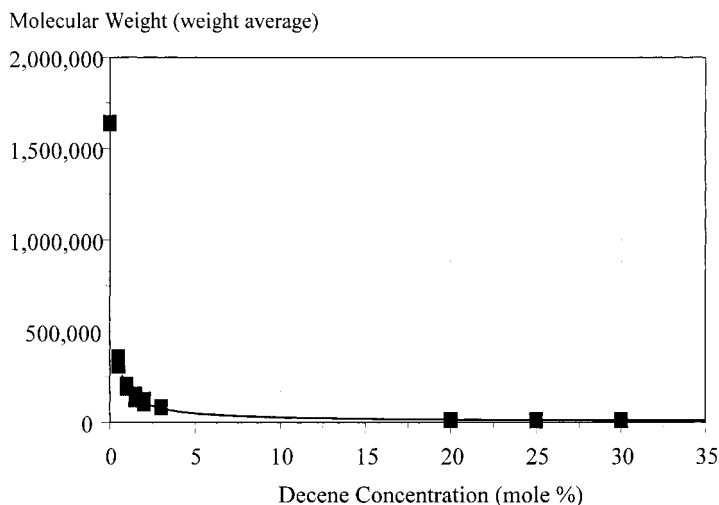


Fig. 4.11 Effect of 1-decene concentration on poly(norbornene) MW (naked nickel catalyst).

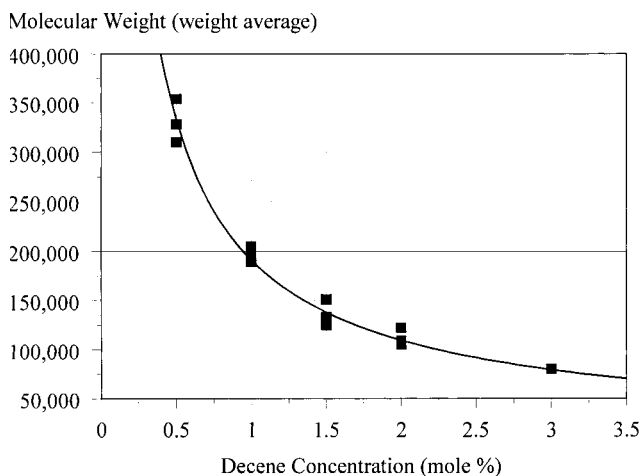


Fig. 4.12 Effect of 1-decene concentration on poly(norbornene) MW (naked nickel catalyst) – 50000 to 350000 M_w region.

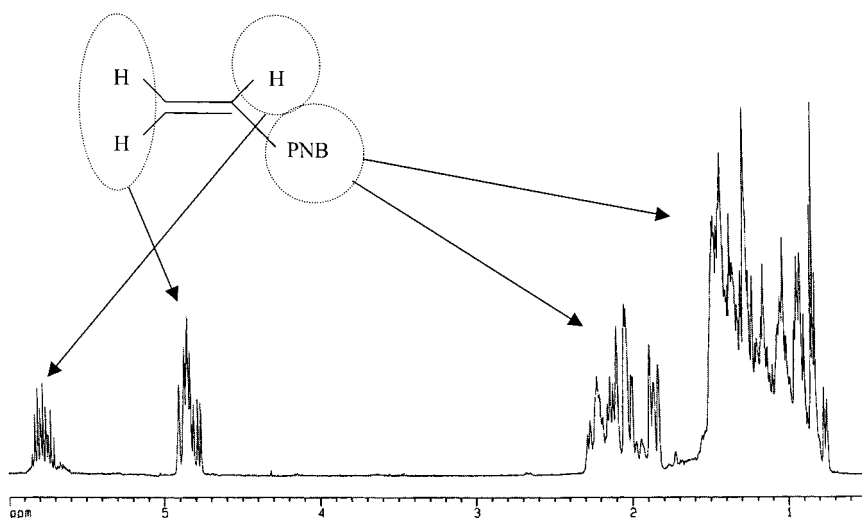


Fig. 4.13 ^1H NMR spectrum of low molecular weight poly(norbornene) made using ethylene as a chain transfer agent.

end group on each poly(norbornene) chain. Correlations from these two groups of vinyl proton signals to downfield olefinic carbon resonances are found in the 2D heteronuclear correlation spectrum.

Having elucidated the end group structure for norbornene polymerized in the presence of ethylene, a catalytic cycle showing initiation, propagation, and chain transfer can be constructed (Fig. 4.14).

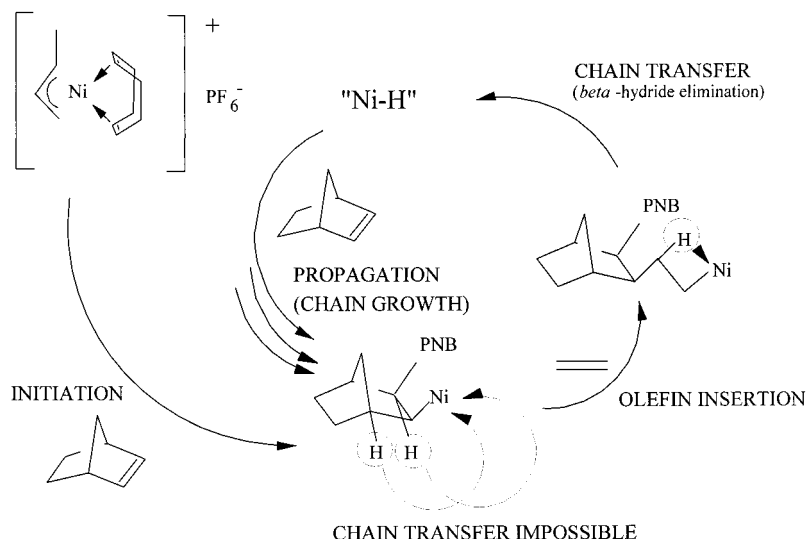


Fig. 4.14 Catalytic cycle for initiation, propagation and chain transfer.

As explained previously, the initiation step occurs exclusively via addition of the allyl ligand to the exo-face of norbornene. From the NMR spectra of the resulting poly(norbornene), the propagation process ("chain growth") occurs likewise. The result of this growth process is a *very* high molecular weight poly(norbornene) since the "normal" mode of chain transfer (β -hydrogen elimination) is not possible, given the geometry of the active, growing center. Notably there are two β -hydrogens, but neither of them can be eliminated to the metal center. One of the two is located at a bridgehead (and is therefore forbidden since its elimination would form a bridgehead olefin and would violate Bredt's Rule) and the other is anti to the metal and therefore is in a conformation unfavorable for β -elimination. Further, should β -hydrogen elimination occur, the resulting end group would be a norbornene unit, which would represent an unfavorable 28 kcal mol^{-1} energy difference over the saturated norbornane structure in the growing polymer chain. However, once an α -olefin is inserted (ethylene is illustrated in Fig. 4.14), β -hydrogen elimination becomes facile and an olefin-terminated poly(norbornene) is formed. The resulting nickel-hydride cation inserts additional norbornene and the catalytic cycle continues. The efficiency with which α -olefins function as chain transfer agents is truly remarkable. Indeed the impact of, for example, 1-decene on the molecular weight of nickel-catalyzed poly(norbornene) could almost be considered catastrophic as can be seen from the data presented in Fig. 4.11. Adding 1 mol% of 1-decene (based on norbornene monomer) causes the molecular weight to drop by an order of magnitude. The efficiency of the chain transfer is clearly a graphic measure of the overwhelming affinity of the naked nickel catalyst for β -hydrogen elimination. It also makes one realize just how remarkable is the fact that norbornene can be polymerized with the same catalyst to such enormous molecular weights ($>1\,000\,000$) in the absence of

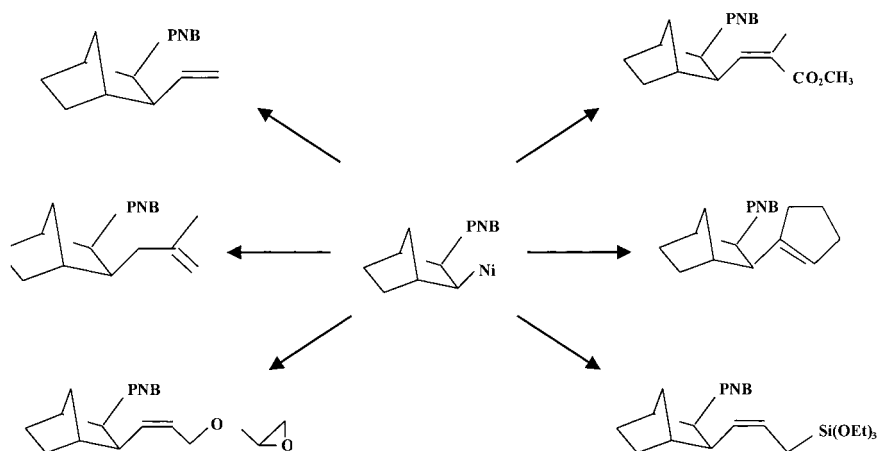


Fig. 4.15 Reactive end-groups formed via chain transfer to olefinic monomers using the naked nickel catalyst.

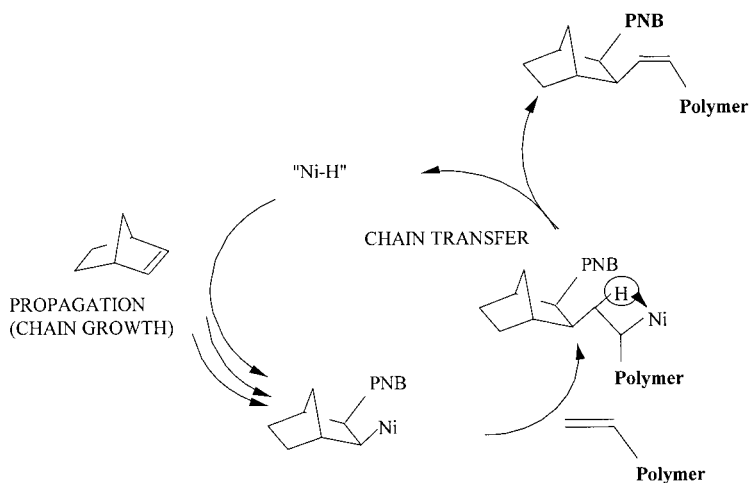


Fig. 4.16 The direct synthesis of A-B block copolymers using the naked nickel catalyst with polymeric chain transfer agents.

α -olefins. In the case of the palladium analogs, α -olefins have little if any effect on MW, presumably indicating that α -olefins cannot compete with norbornene for insertion into the growing palladium-polymer bond.

The extension of this novel chain transfer event to higher molecular weight " α -olefins" has enabled us, and others, to make unique poly(norbornene) block copolymers [44]. Examples of the diversity of this chain transfer chemistry are given in Fig. 4.15 where chain transfer to ethylene, allylglycidyl ether, isobutylene, cyclo-

pentene, methyl methacrylate and cyclopentene all give rise to novel oligomers with reactive end groups.

Fig. 4.16 shows a direct synthesis pathway to A-B block or comb copolymers using the same simple chemistry.

4.2.3.7 Isolation and Characterization of Norbornene Oligomers

Using metallocene catalysts, characterization of oligomers has been used successfully to facilitate the microstructural analysis of poly(cyclic olefins) [45], in the cases of both cyclopentene and norbornene. In these cases hydrogen was applied as chain transfer agent and the resulting products were christened “hydrooligomers”.

Hydrogen is a relatively poor chain transfer agent with the late transition metal catalysts described in this article. In order to obtain oligomers, norbornene was polymerized in the presence of ethylene pressure using naked nickel, catalyst 1. Two peaks (one small and one large) are observed in the GC trace which have m/z 216 and two peaks (one small and one large) are observed which have m/z 244. These two large peaks represent 96% of total intensity of the peaks in this mass range. The m/z s 244 and 216 differ by one ethylene unit and agree with the following chemical formulae: (norbornene)₂(C₂H₄), m/z =216; (norbornene)₂(C₂H₄)₂, m/z =244. Obviously, the small peaks represent compounds that are isomers of the compounds represented by the large peaks.

From mass spectral data alone it is difficult to determine molecular structure or to distinguish between different isomers of the same mass. Therefore, the two norbornene dimers representing 96% of the total were separated and collected by preparative GC and subjected to NMR analysis. The ¹³C NMR spectrum of a mixture of the two dimers is shown in Fig. 4.17, along with the spectra of the dimers after separation.

From the spectra, it is clear that the dimer with m/z 216 is a norbornene dimer terminated with a vinyl group (dimer-4, 113.36 and 141.91 ppm). The compound with m/z 244 is a norbornene dimer with an ethyl and a vinyl group at the “head” (14.11 and 22.18 ppm) and the “tail” (113.72 and 142.87 ppm) of the molecule (dimer-5), respectively. Assignments have been made based on analysis of a ¹³C 2D-INADEQUATE spectrum and are presented in Fig. 4.18. Both dimers are enchain in the 2,3-fashion consistent with the proposal based on the NMR analysis of the norbornene polymer made with “naked nickel”.

The GC/MS of the trimers shows that, just as with the dimers, there are two isomeric trimers observed with an ethyl “head” group and a vinyl “tail” (m/z =338) and two isomeric trimers observed with a hydrogen “head” group and a vinyl “tail” (m/z =310). However with the trimers, the relative concentrations of the isomers are more equal than with the dimers.

The lower molecular weight trimers (m/z =310) were separated and isolated using HPLC techniques. Based on their mass and the structures of the dimers, isomeric forms of vinyl-terminated trimers of norbornene were proposed for these two trimers. This was confirmed by extensive NMR analysis. The ¹H and ¹³C

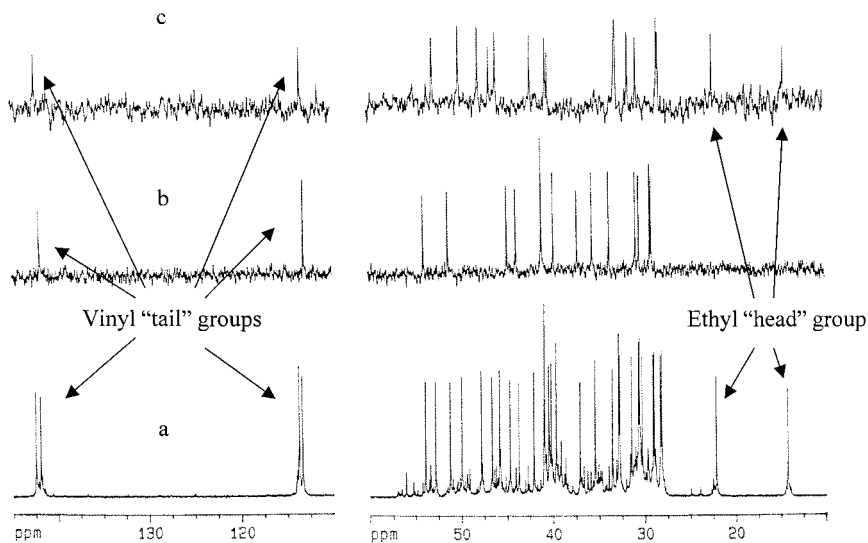
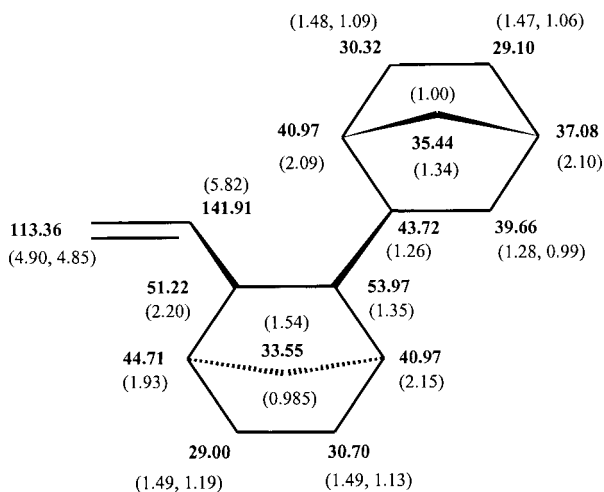
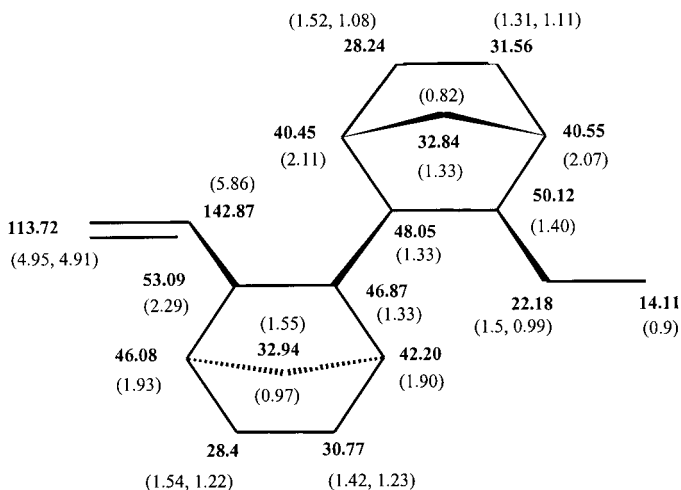


Fig. 4.17 ^{13}C NMR spectrum of dimers **4** and **5** before (a) and after separation (b and c).

NMR assignments for trimer **6** and trimer **7** are shown in Fig. 4.19. Thus the trimers are enchainment in a 2,3-fashion just as for the dimers and only differ with regard to the enchainment of the third (or last) norbornene unit adjacent to the vinyl terminus. Trimer **6** consists of a *rm* triad of norbornene units, while trimer **7** is an *mm* triad. Presumably, the same is true for the two trimer peaks observed with *m/z* 338 (ethyl “head” group and a vinyl “tail”); one consists of the *rm* triad of norbornenes and the other the *mm*.

Given the oligomer results, a modified catalytic cycle can be constructed for the dimerization and trimerization of norbornene using the nickel catalyst in the presence of ethylene (see Fig. 4.20).

A cationic nickel-hydride is the proposed catalytically active species. Insertion of norbornene results in the nickel-norbornyl cationic intermediate, where R is H originating from the nickel-hydride. Under the conditions employed, ethylene insertion is competitive with the first norbornene insertion, followed by norbornene insertion to yield the nickel-norbornyl intermediate where R is ethyl. The second norbornene insertion is stereoselective; about 96% of the time a meso enchainment results. Insertion of ethylene, followed by β -hydrogen elimination forms dimers **4** and **5** (as well as 4% of the isomeric *rac* dimers). Insertion of the third norbornene is non-stereoselective or random; the trimeric product of *meso* or *rac* insertion is isolated after ethylene insertion and β -hydrogen elimination (trimers **6** and **7**, where R=H, along with the trimers where R=ethyl). Extrapolation of the random insertion of norbornene observed in the trimers to the high polymer predicts that the nickel-based poly(norbornene) is best described as atactic which should result in a more soluble polymer than a more regular poly(norbornene).

**Dimer 4****Dimer 5****Fig. 4.18** Structure of dimers 4 and 5, ^{13}C and ^1H chemical shifts, and assignments.

Solid state CPMAS ^{13}C NMR of poly(norbornene) made with naked nickel is identical to that subsequently reported by Arndt [46] in which a Ni(II) acetylacetonate/methaluminoxane catalyst system was used. This polymer was also found to have a low degree of regularity.

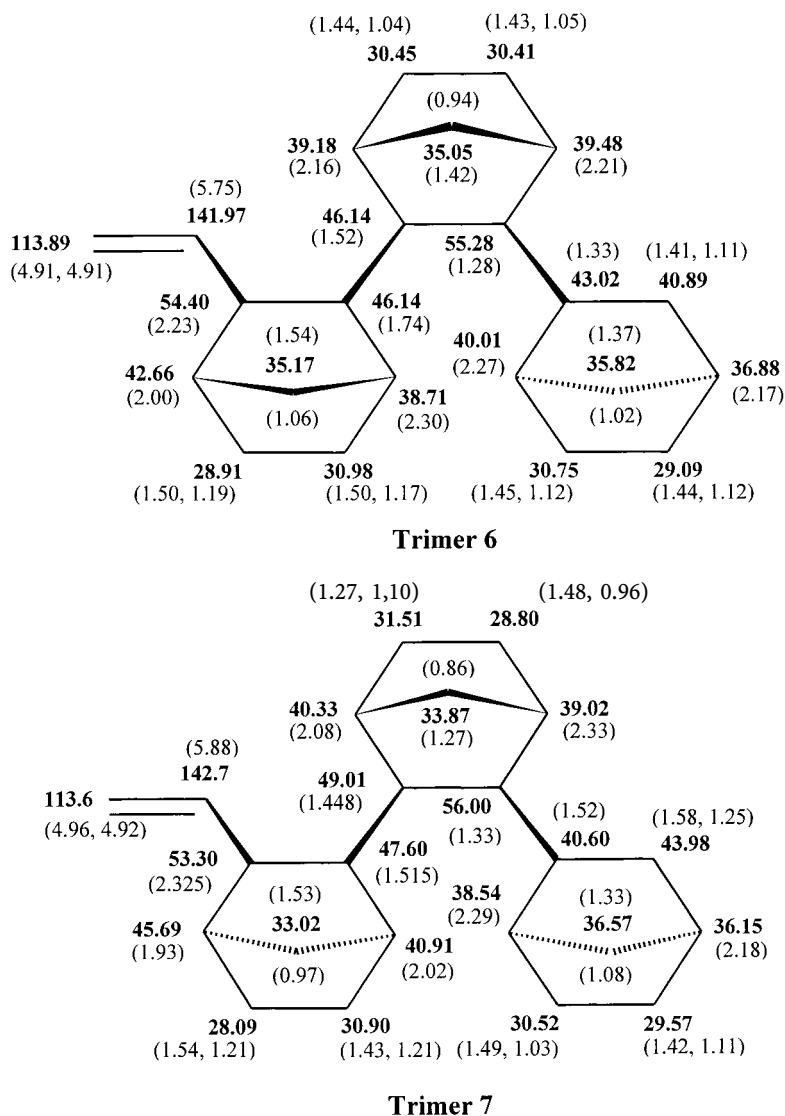


Fig. 4.19 Structures of trimers **6** and **7**, ^{13}C and ^1H chemical shifts, and assignments.

Ludovice and co-workers have determined that polymers made using naked nickel have atactic polymer architecture (i.e., 50% *m* and 50% *r*) [47]. As one examines the scaling exponent of the logarithm of intrinsic viscosity versus the logarithm of molecular weight, one finds a scaling coefficient of 0.5 for the polymer derived from naked nickel which indicates a completely random coil behavior. These results are consistent with the stereochemistry found for the higher oligomers.

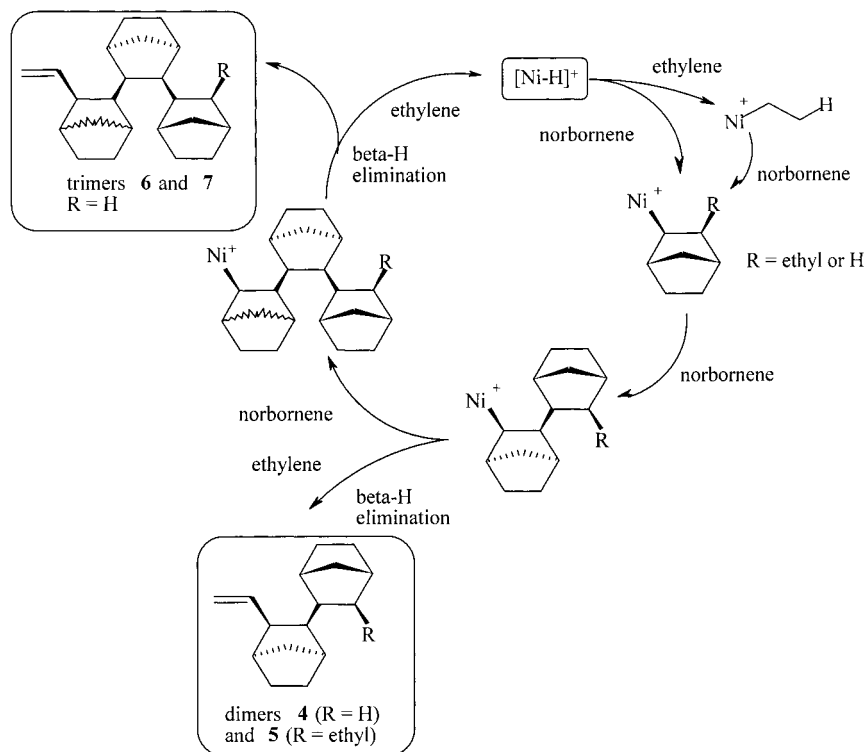


Fig. 4.20 Catalytic cycle for oligomerization of norbornene using ethylene as a chain transfer agent.

To rigorously confirm the microstructure of the oligomers, and by analogy the polymer, crystals of dimer **5** were grown from cold methylene chloride and subjected to single crystal X-ray diffraction analysis. An ORTEP plot of **5** is presented in Fig. 4.21 along with appropriate labeling. The tacticity of this “diad” was determined to be erythro-diisotactic.

4.2.3.8 Control of Glass Transition Temperature

Homopoly(norbornene) possesses an extremely high glass transition temperature of around 370–390°C. While this high T_g endows the polymer with a large number of potentially interesting commercial applications, it also makes it impossible to melt process. Methods were sought to enable the tailoring of the T_g to lower temperatures without necessarily impacting other desirable properties of the polymer such as its high thermal and oxidative stability. It was discovered that using naked nickel, the copolymerization of norbornene with long chain 5-alkylnorbornenes allows the very high T_g of poly(norbornene) homopolymer to be lowered. Higher levels of 5-alkylnorbornene co-monomers result in lower T_g s and, at any

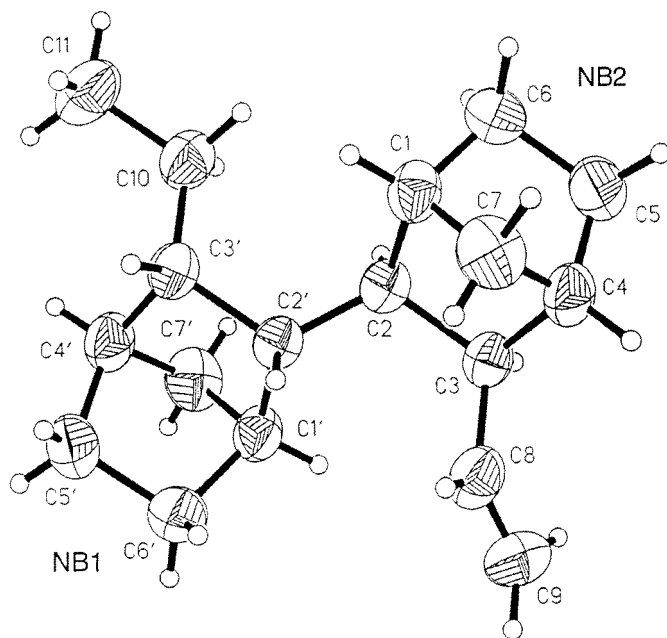


Fig. 4.21 ORTEP representation of dimer 5.

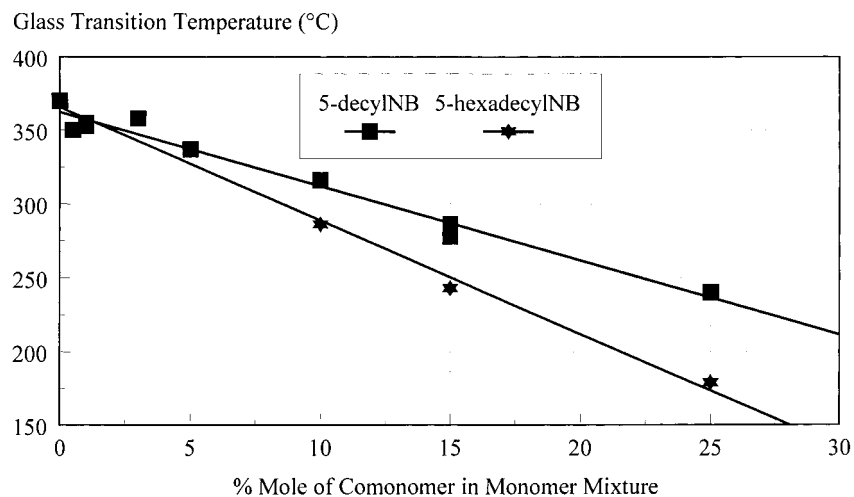


Fig. 4.22 Effect of co-monomers on the T_g of poly(norbornene).

given level (mol%) of co-monomer, the longer the alkyl chain the lower the T_g . Typical results using naked nickel for the copolymerization of norbornene with varying levels of 5-decylnorbornene are presented in Tab. 4.1. The exact T_g depends on the molecular weight of the polymer as well as the composition. For example, runs 4, 8, and 9 yielded polymer with similar glass transition temperatures: 265–285 °C. However, the lower T_g is achieved in two different ways: either by incorporating substantial quantities 5-decylnorbornene (run 4), by lowering the molecular weight (run 9), or both (run 8). The effect of mol% 5-decylnorbornene on T_g is given in Fig. 4.22 for copolymers of similar molecular weights.

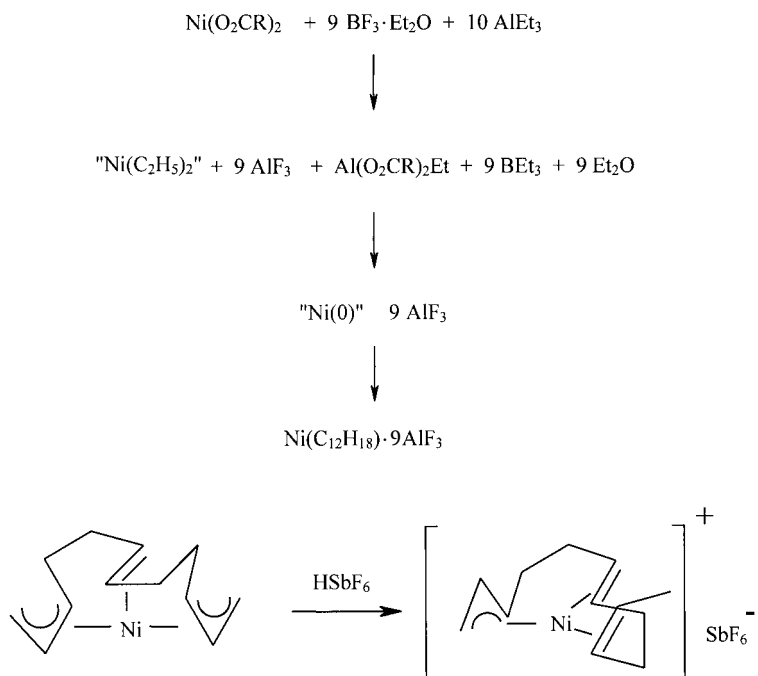
The T_g of the resulting polymers can be steered in this way to any desired value between the T_g of the two homopolymers involved by adjusting the level of co-monomer employed. The T_g of homo(polynorbornene) is around 370–390 °C. The measured T_g of 5-decylnorbornene homopolymer is around 150–160 °C. Longer alkyl substituents (e.g. hexadecylnorbornene) have a more pronounced impact on T_g .

4.2.3.9 Multi-Component Catalyst Systems

Having found active single-component catalysts we sought more cost-effective systems, and systems which were more effective in the copolymerization of 5-alkylnorbornenes (which significantly reduce the effectiveness of the naked nickel catalyst when higher levels of the co-monomer are employed). We quickly discovered that a large variety of “multi-component” or “Ziegler-type” catalyst systems based on simple nickel salts showed good activity in the polymerization of norbornene and alkyl-substituted norbornenes. The simplest systems of all comprised nickel salts in combination with alkylaluminum halides. The preferred alkylaluminum halides are the more Lewis acidic compounds, such as ethylaluminum dichloride, or other alkylaluminums in the presence of chlorinating agents such as hexachloroacetone. Presumably the net effect of the catalyst components is to generate an alkylated cationic nickel species in combination with a weakly coordinating chlorinated aluminum anion.

Particularly effective were the multi-component nickel systems derived from a commercial catalyst first described and developed by Bridgestone Tire Company for the manufacture of to make *cis*-1,4-polybutadiene [48]. The Bridgestone system is the reaction product of $\text{Ni}(\text{O}_2\text{CR})_2$ (R =2-ethylhexyl), $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and AlEt_3 . Our interest was drawn to this system by the elegant mechanistic studies of Taube [32] who, for around 20 years, has studied model compounds in an attempt at understanding the nature of the active species in the industrial catalyst system. The reaction of $\text{Ni}(\text{O}_2\text{CR})_2$, $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and AlEt_3 in a 1:9:10 molar ratio is thought to initially form an unstable $\text{Ni}(\text{C}_2\text{H}_5)_2$ intermediate along with AlF_3 which acts as a colloidal support for the co-formed nickel species. The $\text{Ni}(\text{C}_2\text{H}_5)_2$ intermediate decomposes to form $\text{Ni}(0)$, along with ethylene and ethane. The $\text{Ni}(0)$ reacts with butadiene along documented lines to form $\text{Ni}(\text{C}_{12}\text{H}_{18})$. This catalyst formation chemistry is presented in Scheme 4.1.

The $\text{C}_{12}\text{H}_{18}$ ligand is formed from trimerization of butadiene and is composed of two allyl functions and one olefin moiety. These functionalities coordinate to



Scheme 4.1 Multi-component catalyst for norbornene polymerization.

the Ni to form a “wrap-around” ligand. This complex, while being highly active for butadiene polymerization in toluene (10^4 turnovers), is completely inactive toward norbornene polymerization under the same conditions. If the reaction diluent is changed from toluene to 1,2-dichloroethane (presumably favoring the formation of an unidentified ionic species) good yields of poly(norbornene) are obtained (70%) in a reaction time of 60 min at ambient temperature. However, if hexafluoroantimonic acid (1:1 molar ratio on nickel) is added to the system, a highly exothermic reaction ensues and the yield of polymer under otherwise similar conditions becomes quantitative within 2–3 min.

The reaction of HSbF_6 with $\text{Ni}(\text{C}_{12}\text{H}_{18})$ has been reported to form cationic $[\text{Ni}(\text{C}_{12}\text{H}_{19})]\text{SbF}_6$, wherein the C_{12} wrap-around ligand has been protonated to yield a single allyl and two olefin moieties [49]. Note the structural similarities between this complex (Scheme 4.1) and the naked nickel complex (Fig. 4.4).

The cationic complex, $[\text{Ni}(\text{C}_{12}\text{H}_{19})]\text{SbF}_6$ can be made independently from $\text{Ni}(\text{cyclo-1,5-octadiene})_2$, butadiene, and HSbF_6 . This material exhibited similarly high activity toward norbornene polymerization.

Ultimately it was discovered that introduction of butadiene into the catalyst system was not necessary. Simply adding an equimolar mixture of HSbF_6 to $\text{Ni}(\text{O}_2\text{CR})_2$ in 1,2-dichloroethane solution of norbornene-type monomers followed by introduction of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and AlEt_3 (1:9:10 Ni:B:Al molar ratio) produced an

active catalyst *in situ* that performed as well as naked nickel for norbornene homopolymerization. However, for copolymerizations, especially with higher levels of alkylnorbornenes, the multi-component catalyst performed significantly better than naked nickel, giving good to excellent conversions even at almost a 50:50 molar ratio of norbornene and 5-decylnorbornene.

It was also found that the multi-component catalyst system performed essentially identically to naked nickel in terms of molecular weight control upon addition of the chain transfer agent 1-decene (see Fig. 4.23 and compare to Fig. 4.12).

Moreover, the microstructure of the norbornene homopolymer that is formed using this multi-component catalyst is identical to that produced by naked nickel as evidenced by ^1H and ^{13}C NMR spectroscopy. Based on these observations, it is clear that the active catalyst formed *in situ* from the multi-component system is very similar to the naked nickel single component catalyst [50].

The fact that the multi-component system is more effective at polymerization of 5-alkylnorbornenes may well be attributable to the interaction of amorphous AlF_3 with SbF_6^- forming a larger, more weakly coordinating anion. Much the same argument has been put forth to explain the high activity and high regioselectivity of the multi-component Bridgestone butadiene polymerization system [32].

In an attempt to broaden the scope of this discovery, the efficacy of several other Lewis acids was explored, including the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. Tris(pentafluorophenyl)borane [51] is a very strong Lewis acid and as such is effective in a number of chemical transformations [52]. Tris(pentafluorophenyl)borane probably

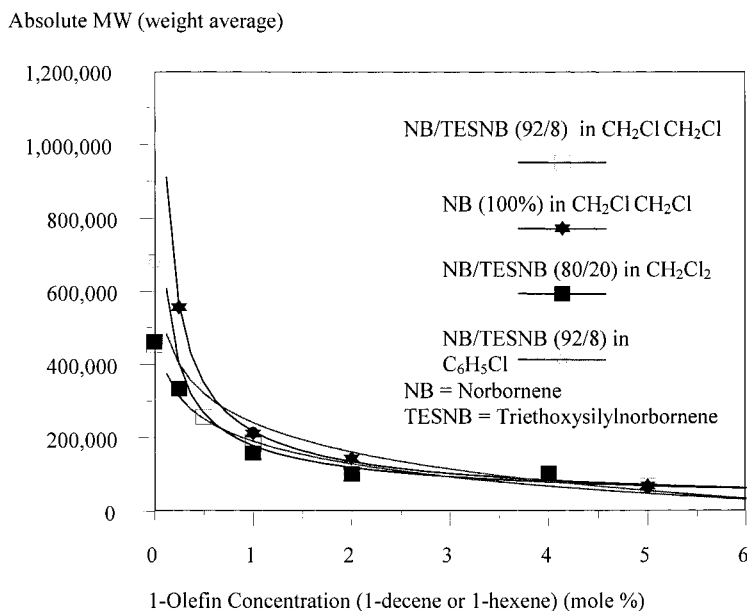


Fig. 4.23 Effect of 1-olefin chain transfer agents on norbornene polymer M_w using the multicomponent catalyst, $\text{Ni}(\text{O}_2\text{CR})_2 + 9 \text{BEt}_3 \cdot \text{Et}_2\text{O} + 10 \text{AlEt}_3$.

has found most utility as an activator in olefin polymerization. Marks and co-workers have shown that $\text{B}(\text{C}_6\text{F}_5)_3$ can abstract the methyl group from $(\text{Me}_5\text{C}_5)_2\text{ZrMe}_2$ to form a cationic zirconocene complex [53]. Following this logic, we investigated mixtures of an organic soluble nickel salt such as $\text{Ni}(\text{2,2,6,6-tetramethyl-3,5-heptanedionate})_2$ (or $\text{Ni}(\text{dpm})_2$) (Fig. 4.24), AlEt_3 , and $\text{B}(\text{C}_6\text{F}_5)_3$ as catalyst components for the polymerization of norbornene.

The thought here was that AlEt_3 would alkylate nickel and $\text{B}(\text{C}_6\text{F}_5)_3$ would then abstract an anionic ligand and form a cationic nickel which should be active in polymerization. Indeed the expected result was found in early experiments using $\text{Ni}(\text{ethylhexanoate})_2$ as the nickel salt in the homopolymerization of norbornene. A significant advantage of this new catalyst system is that, unlike naked nickel which requires the use of chlorohydrocarbon solvents, it is a highly effective polymerization catalyst in aliphatic hydrocarbons. However, as the program developed we investigated the copolymerization of various polar monomers (e.g. ethyl vinyl ether, caprolactone) with norbornene using the same catalyst. The ^1H NMR spectrum of the material isolated was very different from naked nickel homopolynorbornene and we quickly recognized that the oxygenated monomers must be acting as ligands, apparently changing the ligand field around the active center and thereby modifying the PNB microstructure. As discussed later, the ^{13}C NMR and 2D-COSY NMR confirmed a new PNB microstructure. We also saw the same new microstructure when the catalyst was used to copolymerize norbornene with 5-triethoxysilylnorbornene, which caused us to investigate homopolymerizing norbornene in the presence of catalytic amounts (5–20 moles per mole nickel) of alkoxysilanes such as tetraethoxysilane (TEOS). The resulting polymers also exhibited the new PNB microstructure, indicating clearly that oxygen donors are giving rise to a new, different active center. We found that a large number of oxygen ligands were viable, ranging from TEOS, to simple alkoxysilanes, ethers including chelating diethers, esters and even alcohols or water. The preferred solvents were found to be simple hydrocarbons such as toluene and cyclohexane. Halohydrocarbons such as dichloroethane (DCE) favored the formation of naked nickel type of microstructure, although excess oxygen ligand (e.g. >5–10 moles TEOS per mole Ni) gave rise to the new PNB form.

In the course of this work we found the true transformation that was ultimately responsible for the formation of the active species to be entirely unexpected, namely the transfer of C_6F_5 groups from boron to nickel (see below) and that oxygen donors appear to mediate or catalyze this transfer.

Tab. 4.2 lists several norbornene polymerization experiments.

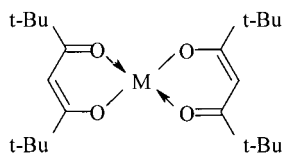


Fig. 4.24 $\text{Ni}(\text{2,2,6,6-tetramethyl-3,5-heptanedionate})_2$ (or $\text{Ni}(\text{dpm})_2$).

Tab. 4.2 Polymerization of norbornene using multicomponent catalyst systems.

Run ^{a)}	Nickel complex	Co-catalyst	Activator	Conversion [%]	Activity ^{b)}	M_w	M_w/M_n
1	Ni(dpm) ₂ 0.22 mM	AlEt ₃ 2.2 mM	B(C ₆ F ₅) ₃ 2.0 mM	97	373 000 ^c	1 050 000 ^{d, e)}	5.95
2		–		95	366 000 ^{c)}	619 000 ^{e)}	2.40
3		–	B(C ₆ F ₅) ₃ 0.22 mM	48	186 000	–	–
4		–		54	206 000	–	–
5		–		46	178 000	–	–
6	Pd(dpm) ₂ 0.22 mM	–	B(C ₆ F ₅) ₃ 2.0 mM	95	insoluble	–	–
7	Pd(dpm) ₂ 0.22 mM	–	B(C ₆ F ₅) ₃ 0.22 mM	11	–	–	–
8		–	BF ₃ · Et ₂ O 2.0 mM	0 ^{f)}	–	–	–
9		–	B(OEt) ₃ 2.0 mM	0	–	–	–
10		–	B(OC ₆ F ₅) ₃ 2.0 mM	0	–	–	–
11	Ni(dpm) ₂ 0.22 mM	–	B(C ₆ F ₅) ₃ · 3 H ₂ O 0.22 mM	91	352 000	418 000	2.43
12		–		87	331 000	314 000	1.73

a) All runs were carried out in 1,2-dichloroethane for 1 h at room temperature at 0.9 M norbornene concentration.

b) g polymer produced (mol Ni h)^{–1}.

c) Likely to be much higher since a puck formed within 1 min of mixing.

d) Not completely dissolved.

e) Partially excluded from column.

f) No high polymer obtained upon addition to methanol [55].

All experiments were conducted at room temperature for 1 h. In run number 1, the catalyst was a mixture of Ni(dpm)₂, AlEt₃, and B(C₆F₅)₃ in a 4000:1:10:9 norbornene:Ni:Al:B molar ratio. High conversion (97%) and activity was achieved. In fact, the activity observed is in all likelihood much higher than the calculated 373.00 g of polymer obtained per mol nickel metal per hour, since the polymerization reaction formed a puck within one minute of addition of the catalyst components and polymerization conversion was determined only after an hour. The molecular weight of the polymer obtained is extremely high, but the actual molecular weight data should be viewed with some skepticism since the sample was not completely soluble in trichlorobenzene at 135 °C and was partially excluded from the GPC column.

¹H NMR analysis of the polymer obtained from run 1 unambiguously showed that the polymer is of the addition type since no double bond resonances are observed. Its ¹³C NMR spectrum shows that it is exo enchainned. The spectrum does

not exhibit resonances in the 20 to 24 ppm region. The presence of such resonances has been taken as evidence of endo enchainment based on model studies [54]. In this regard the polymer from run 1 is similar to that produced using $[(\eta^3\text{-crotyl})\text{Ni}(1,5\text{-COD})]\text{PF}_6$ ("naked nickel", see Section 4.2.3.4).

However, it was also clear, based on NMR studies, that the type of addition polymer formed in run 1 was quite different from that produced using, for example, $[(\eta^3\text{-crotyl})\text{Ni}(1,5\text{-COD})]\text{PF}_6$. A comparison of the polymer ^1H NMR spectra is given in Fig. 4.25. Note the dissimilarity between the two spectra. The same is true of their ^{13}C NMR spectra. The formation of a catalyst unique and distinct from $[(\eta^3\text{-crotyl})\text{Ni}(1,5\text{-COD})]\text{PF}_6$ by the reaction of nickel(2,2,6,6-tetramethyl-3,5-heptanedionate) $_2$ or $\text{Ni}(\text{dpm})_2$, AlEt_3 , and $\text{B}(\text{C}_6\text{F}_5)_3$ would be consistent with the production of poly(norbornene) exhibiting different NMR spectra and apparently different microstructures.

Further evidence supporting the creation of a unique type of active species was obtained upon discovering that it was entirely *unnecessary* to add AlEt_3 to the reaction mixture to obtain excellent yields of polymer. In run 2, 95% conversion and a very high activity was obtained when a 4000:1:9 norbornene:Ni: $\text{B}(\text{C}_6\text{F}_5)_3$ molar ratio was employed. Evidently, an electron-withdrawing aryl substituent is necessary for creation of the active species since neither $\text{BF}_3 \cdot \text{Et}_2\text{O}$, $\text{B}(\text{OEt})_3$, nor $\text{B}(\text{OC}_6\text{F}_5)_3$ in combination with $\text{Ni}(\text{dpm})_2$ yielded polymer upon attempted precipitation with methanol.

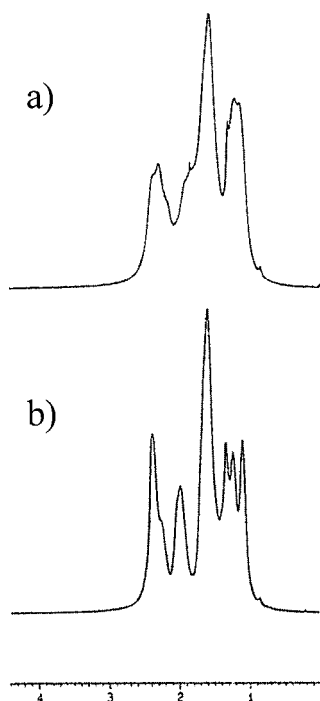


Fig. 4.25 ^1H NMR spectra of addition poly(norbornene) made with naked nickel (a) and made with $\text{Ni}(\text{dpm})_2$, AlEt_3 , and $\text{B}(\text{C}_6\text{F}_5)_3$ (b).

Polymerization experiments carried out using $\text{Pd}(\text{dpm})_2$ also showed that norbornene was polymerized quite effectively in the absence of AlEt_3 at a 4000:1:9 monomer: Pd : $\text{B}(\text{C}_6\text{F}_5)_3$ ratio (run 6, Tab. 4.2). The polymer was soluble enough at 50°C in *ortho*-dichlorobenzene to obtain a ^1H NMR spectrum. No olefinic resonances were observed, confirming the formation of addition poly(norbornene). However, the solubility difficulties encountered prevented further characterization.

Our search for a more active system led us to bis(pentafluorophenyl)nickel complexes originally reported by Klabunde and co-workers in the 1980s [56]. One of the more interesting complexes reported was $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ (Fig. 4.26). Toluene can be readily replaced by a number of neutral electron donors including xylene, mesitylene, THF, PEt_3 , and norbornadiene. In fact, Klabunde noted that formation of $(\text{norbornadiene})\text{Ni}(\text{C}_6\text{F}_5)_2$ was accompanied by intractable polymer. Klabunde speculated that vinyl addition polymerization occurred with possible cross-linking. Unfortunately, the insolubility of the norbornadiene polymer prevented further analysis.

Thus, we synthesized and tested this toluene complex and found that it does indeed effect the polymerization of norbornene-type monomers. Polymerization of norbornene-type monomers is not restricted to nickel complexes containing C_6F_5 ligands. We have found that the electron-withdrawing tris(2,4,6-trifluoromethylphenyl) ligand [57] is also quite effective in polymerizing both norbornene and 5-triethoxysilylnorbornene, for example. At a 4000:1 monomer to nickel ratio, $\text{Ni}[\text{2,4,6-tris(trifluoromethyl)phenyl}]_2(1,2\text{-dimethoxyethane})$ (Fig. 4.27) gave 37% conversion into polymer from an 80:20 norbornene:5-triethoxysilylnorbornene monomer mixture.

Thus, we discovered the unusual activation of nickel toward the polymerization of norbornene-type monomers by C_6F_5 transfer from $\text{B}(\text{C}_6\text{F}_5)_3$ to nickel [58], a reaction pathway that is typically a decomposition route for transition metal catalysts [59]. This discovery led to the development of a class of neutral, single-site nickel complexes containing electron-withdrawing group such as C_6F_5 that are effective for the polymerization of norbornene-type monomers.

The most direct proof of the initiation mechanism would come from elucidation of the head group structure of the polymer produced using $(\eta^6\text{-toluene})$ -

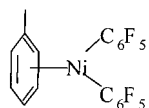


Fig. 4.26 Neutral bis(pentafluorophenyl)nickel initiator for the polymerization of norbornenes.

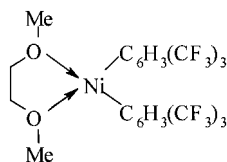


Fig. 4.27 $\text{Ni}[\text{2,4,6-tris(trifluoromethyl)phenyl}]_2(1,2\text{-dimethoxyethane})$.

$\text{Ni}(\text{C}_6\text{F}_5)_2$. In an effort to lower the molecular weight of the polymer chain and simplify analytical characterization, homopolymerization of norbornene was carried out in the presence of ethylene pressure. Norbornene polymerizations catalyzed by cationic nickel catalysts such as $[(\eta^3\text{-crotyl})\text{Ni}(\text{1,5-COD})]\text{PF}_6$ are quite susceptible to acyclic olefins as chain transfer agents and produce substantially reduced molecular weight vinyl-terminated poly(norbornenes) (Section 4.2.3.5).

Thus, norbornene was polymerized under 5 psig ethylene on a 5 g scale using $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ at a 500:1 norbornene to nickel molar ratio. The polymer was precipitated into methanol and a low yield (8%) of solid was collected by centrifugation. The methanol solution was evaporated to dryness and a smaller amount of a methanol soluble fraction was collected. Although the yield of the methanol-insoluble fraction was low, NMR analysis of this fraction was quite informative. While the aliphatic region of the ^1H NMR spectrum was identical to the higher molecular weight polymer, there were three new resonances observed: broad singlets at 3.3 and 5.0 ppm and a pair of broad singlets at 5.7 and 6.0 ppm. The relative intensities of these signals were about 1:2:1, respectively. The two downfield resonances are consistent with vinyl groups at the end of the polymer chain. The assignment of the resonance at 3.3 ppm was not clear at this stage of our investigation and required further analysis (see below).

The ^{19}F NMR spectrum of the methanol-insoluble fraction was especially illuminating. Four distinct groups of resonances were observed: singlets at -162.7 (2 F), -158.1 (1 F), and -139.3 (1 F), and two signals at -133.1 and -133.8 (1 F). These resonances were consistent with the presence of a C_6F_5 group appended to the polymer, presumably at the head of the polynorbornene chain.

The methanol-soluble fraction was of sufficiently low molecular weight that peaks could be observed in the field ionization mass spectrometry experiment. Analysis of the predominant series of peaks were consistent with the structure shown in Fig. 4.28, where the end and head groups are $-\text{CH}=\text{CH}_2$ and $-\text{C}_6\text{F}_5$ and $n=2, 3, 4, 5, 6$, and 7 ($m/z=382, 476, 570, 664, 758$ and 852 , respectively). The ^1H and ^{19}F NMR spectra confirmed the presence of vinyl and pentafluorophenyl groups in the methanol-soluble fraction.

Exact assignment of the resonances observed in the ^{19}F , ^1H and ^{13}C NMR spectra of the norbornene oligomers required separation of each member of the series. First, norbornene polymerization with $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ in the presence

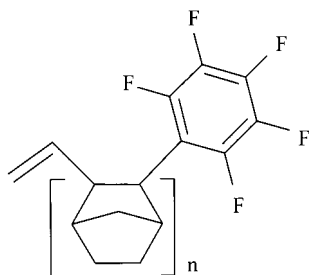


Fig. 4.28 Norbornene oligomers made using bis(pentafluorophenyl)nickel.

of 5 psig ethylene was scaled up to 25 g. Again methanol-soluble and -insoluble fractions were obtained. The soluble fraction was further fractionated using liquid chromatographic techniques. Sufficient quantities of the dimer, trimer, tetramer and pentamer fractions were isolated for NMR investigation.

The ^{19}F NMR spectra for each fraction are shown in Fig. 4.29.

In the dimer fraction there are two isomers present in an approximate 2 to 1 ratio (fraction a). The major isomer exhibits signals at ca. -136.0 , -140.8 ppm, -158.4 , and -163.6 , while for the minor isomer signals are observed at ca. -136.8 , -137.3 , -153.8 , and -164 ppm. The first trimer fraction contained only one isomer (fraction b) while the second trimer fraction consisted of yet two more isomers distinct from the first trimer (fraction c). This pattern was repeated for the tetramer fractions. The first tetramer fraction consisted of only one isomer (fraction d) while the second tetramer fraction contained two more distinct tetramer isomers (fraction e). A much smaller amount of the pentamer was isolated which accounts for the poor signal to noise observed in its spectrum (fraction f).

The ^{19}F NMR spectra of the fractions mimic what was observed for the higher molecular weight oligomers in that four resonances are present in a 1:1:1:2 intensity ratio. This is easily explained if one considers an exo-enchainment pentafluorophenyl head group (see Fig. 4.28). In the spectrum of the single trimer isomer (fraction

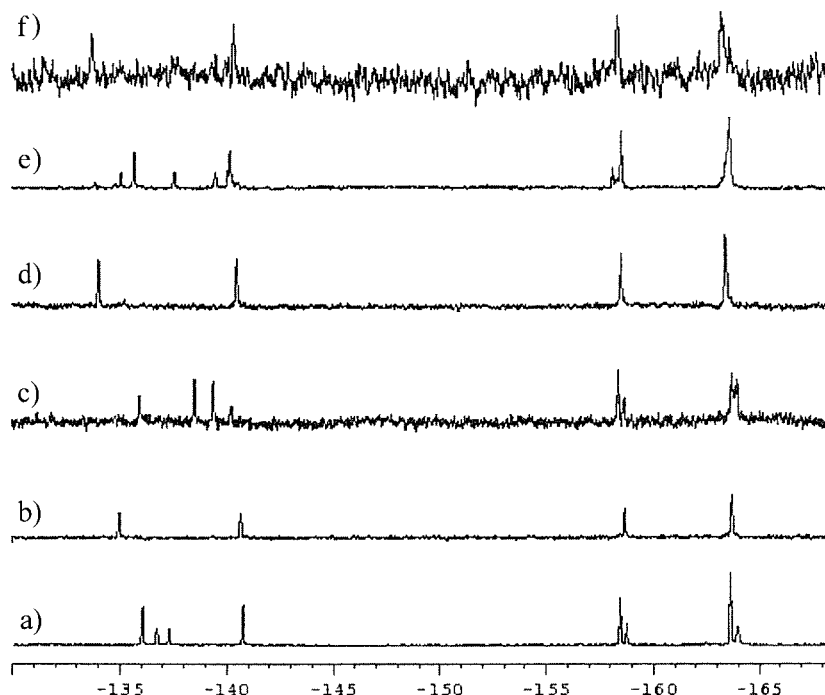


Fig. 4.29 ^{19}F NMR spectra of oligomer fractions a (dimers), b (trimer), c (trimers), d (tetramer), e (tetramers), f (pentamer).

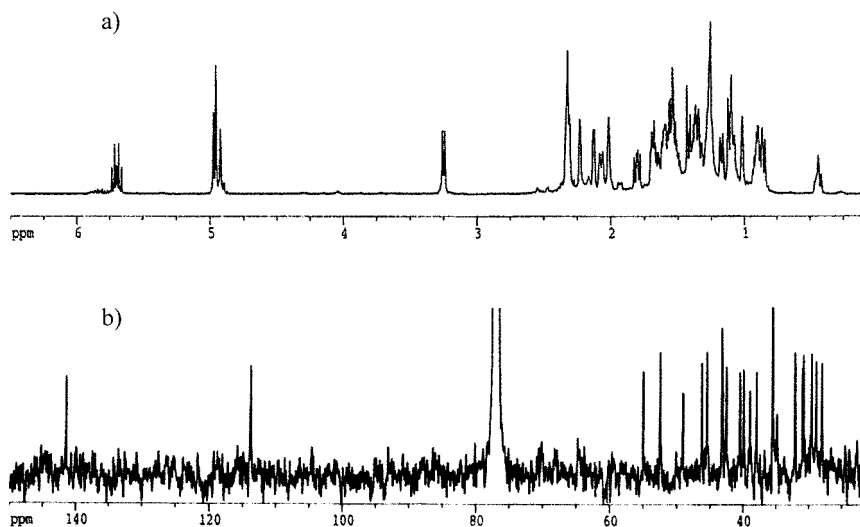


Fig. 4.30 (a) ^1H NMR spectrum of trimer in fraction b. (b) ^{13}C NMR spectrum of trimer in fraction b in CDCl_3 .

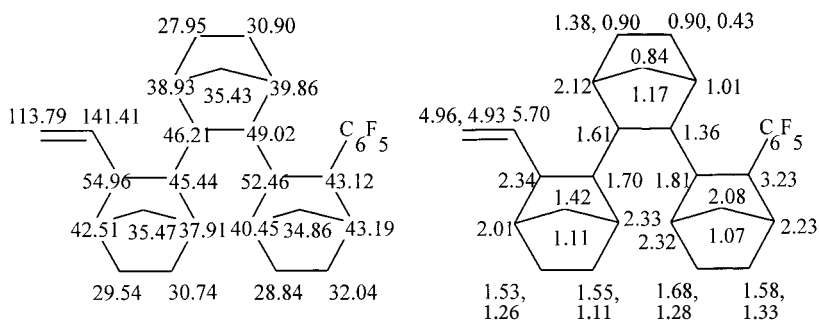
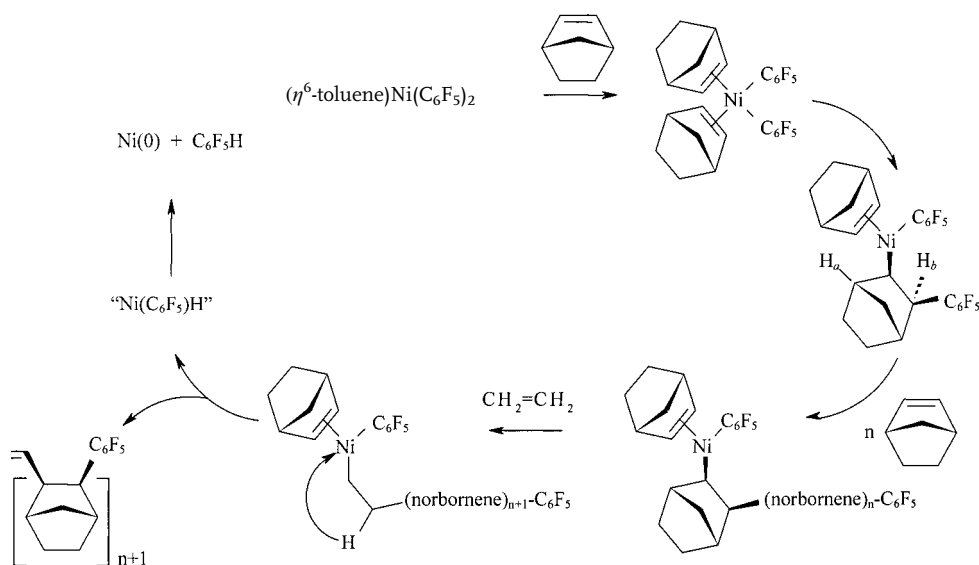


Fig. 4.31 ^{13}C and ^1H NMR assignments for the trimer in fraction b.

b, Fig. 4.29), for example, the para-fluorine is assigned to the peak at -158.6 ppm. The two ortho-fluorines should be inequivalent. One fluorine is syn to the norbornene-bridging methylene and the other is anti. In fact two resonances at -135.0 and -140.8 ppm are observed and are assigned to the two ortho-fluorines. The two meta-fluorines which theoretically should also be inequivalent are evidently accidentally degenerate and resonate at -163.8 ppm [60]. Complete assignment of chemical shifts in the ^{19}F , ^1H and ^{13}C spectra for each fraction was made using a variety of 1D and 2D NMR techniques. The ^1H and ^{13}C spectra for the trimer in fraction b appear in Fig. 4.30 and the full assignments are shown in Fig. 4.31.

Mechanism

The isolation, separation and unambiguous characterization of the end group in a series of norbornene oligomers synthesized using $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ in the presence of ethylene enabled us to construct a mechanism of chain initiation and termination (see Scheme 4.2). The fact that each isolated norbornene oligomer contained a C_6F_5 head group and a vinyl end group supports the hypothesis that initiation of the norbornene polymer chain occurs via insertion of the exo face of the norbornene monomer into the Ni–C bond of the C_6F_5 ligand. Presumably, coordination of norbornene to Ni occurs prior to insertion.



Scheme 4.2 Norbornene oligomerization using bis(pentafluorophenyl)nickel.

After the first norbornene insertion, propagation ensues and molecular weights grow to large values suggesting that no chain termination occurs. For cationic nickel catalysts such as $[(\eta^3\text{-crotyl})\text{Ni}(1,5\text{-COD})]\text{PF}_6$, similar behavior was observed since β -hydrogens were unavailable for elimination. It appears that this also applies here. H_a is in a bridgehead position and its elimination would violate Bredt's rule by forming a bridgehead double bond. H_b is anti to Ni and is improperly oriented for elimination.

After insertion of ethylene occurs, presumably subsequent to coordination to Ni, a $(\text{C}_6\text{F}_5)\text{Ni-CH}_2\text{-CH}_2$ -capped norbornene polymer intermediate is formed. Free rotation about the $\text{-CH}_2\text{-CH}_2\text{-}$ bond of this intermediate offers two β -hydrogens that can be readily eliminated to form a neutral $\text{NiH}(\text{C}_6\text{F}_5)$ species and a vinyl-terminated polynorbornene chain. A similar hydride intermediate has been proposed by Klabunde for the dimerization of ethylene and propylene [61].

The fate of the neutral $\text{NiH}(\text{C}_6\text{F}_5)$ species became of primary interest. If this species were capable of coordinating and inserting norbornene into the Ni–H bond many turnovers could be attained. However, it appears that under the conditions employed $\text{NiH}(\text{C}_6\text{F}_5)$ was not sufficiently stable to undergo further norbornene polymer initiations. We see no evidence for the formation of hydride-initiated poly(norbornene) chains, i.e., $\text{H}-(\text{norbornene})_n\text{-vinyl}$, by mass spectrometry. The absence of such polymer chains, the formation of black solutions suggestive of nickel metal during norbornene polymerization in the presence of ethylene, and the presence of $\text{C}_6\text{F}_5\text{H}$ in the mass spectrum of the reaction mixture support the notion that the $\text{NiH}(\text{C}_6\text{F}_5)$ moiety decomposes via reductive elimination of pentafluorobenzene and nickel metal.

All of this data suggest strongly that $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ should be thought of as an initiator of norbornene polymerization rather than a catalyst. A full paper describing the chemistry and polymerization performance of this initiator system will be published shortly [62].

Presumably, the key role of the second pentafluorophenyl ligand is to increase the electrophilicity of the nickel center, enhancing the ability of the nickel to coordinate incoming monomer and hence cause polymerization to occur. Although one might well expect a neutral nickel center to generate a different polymer microstructure than does a cationic species, it is possible that the second pentafluorophenyl ligand influences the enchainment of the norbornene monomer units, which apparently is manifested in the microstructure of the polymer. Certainly based on NMR spectra, the microstructure of poly(norbornene) made using $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ is substantially different than that produced from $[(\eta^3\text{-crotlyl})\text{Ni}(1,5\text{-COD})]\text{PF}_6$ (naked nickel). According to Ludovice et al., polymers derived from $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ represent something approximately midway between an atactic structure and an erythro-di-isotactic microstructure having approximately 75% *m* and 25% *r* enchainment [63]. In this publication, the neutral nickel catalyst represents the $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ catalyst system. The identification of both *m* and *r* diads in the oligomer fractions are consistent with this picture.

All of the above research developed from the concept of screening different metal salts with a variety of Lewis acids and organometallic activators (usually simple trialkylaluminums). Having found the above-described dramatic effect of oxygen donor ligands, we sought to investigate other ligands, primarily phosphorus and nitrogen ligands, with the ultimate goal of enabling the copolymerization of norbornene and ethylene with these catalysts (see Sections 4.3.1.1 and 4.3.1.2). In the course of this work we observed that the addition of phosphine ligands, which we had found to deactivate nickel catalysts, dramatically increased the activity of the palladium analogs. Furthermore the use of a phosphine ligand increases the thermal stability of the catalysts allowing the polymerizations to be run at higher temperatures (60–100 °C compared to an optimum temperature of 20–30 °C in the case of naked nickel or naked palladium). The net effect is to increase the productivity of the palladium catalysts by about three orders of magnitude, allowing more than 100 000 moles of norbornene (up to about 1 million moles) to be converted per mole of palladium compared to a sluggish 2000 moles per mole with

naked palladium. The following example from a recent patent application [64] serves to illustrate the very high activity of such catalysts:

To a thick-walled, septum-sealed glass vial, equipped with a magnetic stir-bar was added 5-butylnorbornene (7.95 g, 53 mmol), toluene (19 mL), palladium ethyl hexanoate (82 μ L, 0.35 μ mol), tricyclohexylphosphine (28 μ L, 0.35 μ mol), trispentafluorophenylboron (126 μ L, 6.36 μ mol) and triethylaluminum (4.2 μ L (1.7 M in cyclohexane), 7.0 μ mol) (ratio of monomer to palladium, 150000:1). The resulting stirred solution was placed in a heated oil bath at 67 °C for a total of 3 h. Within less than 30 min the colorless, clear solution was a highly viscous mass that could no longer be stirred. After 3 h the colorless gel was isolated by breaking the flask, was cut into small pieces using a blade and the material was dissolved in boiling toluene (800 mL) over a period of several hours. The polymer was precipitated by pouring into excess methanol (1 L), filtered off and washed with excess methanol prior to drying to constant weight under vacuum at 80 °C. The dried, white, granular polymer was found to weigh 7.76 g (97.6% conversion).

In this patent application are also described many examples of “well-defined” catalysts made by reacting one mole of the desired phosphine with allylpalladium chloride dimer and then activating the resulting complex with a suitable activator. Preferred activators are weakly coordinating anion salts capable of abstracting a halide (e.g. the lithium salt of tetrakis(pentafluorophenyl)borate). The activator is typically applied in a 5 molar excess on palladium to ensure complete activation. Preferred phosphines are hindered, strongly donating examples such as tricyclohexylphosphine and tritolylphosphine. These highly active catalysts also proved to be the ideal systems to allow the realization of RIM (reaction injection molding) of norbornenes to afford completely saturated, high T_g poly(norbornene) parts in a mold (Section 4.2.3.2).

4.2.3.10 Polymerization of Norbornenes Containing Functional Groups

The (co-)polymerization of functional monomers was also explored with the Ni and Pd catalyst systems. The multi-component Ni catalyst ($\text{Ni}(\text{O}_2\text{CR})_2 + \text{HSbF}_6 + 9\text{BF}_3 \cdot \text{Et}_2\text{O} + 10\text{AlEt}_3$) works very well for the copolymerization of norbornene and 5-triethoxysilylnorbornene. The copolymerization of norbornene and with 5–10 mol% 5-triethoxysilylnorbornene monomers yields a high molecular weight copolymer of the same molar composition in excellent yield (85%) at a 4000:1 monomer to nickel molar ratio.

The copolymers of this type were found to have very interesting adhesive, dielectric, and optical properties. The polymers were found to adhere to substrates such as silicon dioxide, aluminum, copper, and even gold. Even more surprisingly, the polymer film cast on gold did not delaminate even after exposure to boiling water for 2 h. The refractive index of this polymer was around 1.51 and the birefringence was low ($\Delta n = 0.0014$). The electrical permittivity was also low (ca. 2.5). All of these properties, coupled with the inherently high glass transition temperature, make the materials attractive for electronic and optical applications [65].

Of all of the functional groups (as substituents on norbornene monomers) that we investigated the triethoxysilyl group was essentially unique with regard to its ability to be readily copolymerized using a variety of different nickel and palladium catalysts. While naked palladium copolymerizes these monomers well, as do a variety of other single- and multi-component palladium catalysts, the activating effect of phosphine ligands (Section 4.2.3.9) again has a dramatic effect on catalyst productivity, illustrated by the following examples:

To a thick-walled, septum-sealed glass vial, equipped with a magnetic stir-bar was added 5-butylnorbornene (7.57 g, 50.4 mmol), triethoxysilylnorbornene (0.68 g, 2.6 mmol), toluene (8 mL), palladium ethyl hexanoate (2.6 μ mol), tricyclohexylphosphine (2.6 μ mol), tris(pentafluorophenyl)boron (23.4 μ mol) and triethylaluminum (26 μ mol) (ratio of monomers to palladium 20000:1). The resulting stirred solution was placed in a heated oil bath at 65 °C. Within 30 s the reaction exothermed violently resulting in a solid mass that no longer stirred within 45 s.

In an identical experiment without the phosphine ligand, no exotherm was observed and little or no reaction ensued. The resulting stirred solution was placed in heated oil bath at 65 °C for a total of 3 h. The resulting polymer was precipitated by pouring into excess acetone, was filtered off and washed with excess acetone prior to drying to constant weight under vacuum at 80 °C. The dried, white polymer was found to weigh less than 0.1 g (less than 1.5% conversion). This shows the dramatic improvement of added phosphine ligands on catalyst performance.

Other functional monomers can also be (co-)polymerized using naked metal catalysts, but almost invariably this requires the use of naked palladium catalysts which we found to have a high tolerance to functional groups including carboxylic acid esters and the like [66].

In the case of the polymers for photoresist applications there is an extreme need for tolerance of functional groups since, as outlined below, every monomer unit contains a functional group. Such extreme conditions dictate the use of a palladium catalyst, if a cationic catalyst is to be employed. However neutral nickel catalysts were also found to have a high tolerance of functional groups (presumably because of the diminished electrophilicity of the nickel center compared to cationic counterparts). Thus, in addition to cationic palladium catalysts, certain neutral nickel species are also highly effective systems [68], in particular species of the type $(L)Ni(Ar^F)_2$ (where L=covalent ligand, Ar^F =fluorinated aryl group). Examples of such initiators include $(\eta^6\text{-toluene})Ni(C_6F_5)_2$ (first reported as an ethylene dimerization catalyst by Klabunde [69]) and $(\text{dimethoxyethane})Ni(3,5\text{-(CF}_3)_2C_6H_3)_2$. Presumably one of the fluorinated aryl groups serves to tune the electrophilicity of the nickel center while the second inserts a norbornene monomer and becomes a polymer head group. These catalysts are discussed in detail in Section 4.2.3.9.

4.2.3.11 Polymer Properties and Applications

The Goodrich polymers are aimed at a number of microelectronic applications and are high-priced specialties [70]. There are three families of products:

- AvatrelTM Dielectric Polymers (low- k dielectric applications such as interlayer dielectrics, passivation layers, die attach adhesives, chip encapsulants (both molding and adhesive) and underfill materials).
- AppearTM Optical Polymers (optical applications such as wave-guides and flat-panel display substrates).
- DuvcorTM Photoresist Polymers (photolithographic applications, primarily deep UV (193 nm and 157 nm) positive photo-resists).

Each of these polymers exploit the ability of the nickel and palladium catalysts described above to tolerate functional groups and to copolymerize norbornene monomers bearing esters etc. into the polymer backbone.

Dielectric Polymers

In 1964, Gordon Moore, co-founder of Intel Corporation, predicted that the number of transistors on a chip would double every 16–18 months. Since then, the semiconductor industry has more or less kept up this feverish pace. In order to take advantage of the advances made in semiconductors, similar improvements need to be made in the other components that make up a complete electronic device. A key component in electronic devices is the package of the integrated circuit (IC or chip). According to Rymaszewski, Tummala, and Watari [71], “Packaged electronics is the embodiment of all electronic equipment – calculators, personal computers, mainframe computers, telephones, television, and so forth... Active components are interconnected, supplied with power, and housed in packaging. Success in a very competitive marketplace hinges on superior performance and price.” Despite the pivotal role that packaging plays in electronics, performance has not kept pace with semiconductors improvements. In the future this disparity is expected to grow.

Bare chip speed has outpaced the packaged chip speed. As pointed out by Doane and Franzon [72], “... chip interconnections play a more dominant and limiting role in determining overall system speed and performance. Packaging of the chips has become a more significant factor in performance. Systems level performance improvements are now being limited more by the packaging and the interconnection technologies, and less by the chip technology itself.”

Given the role of packaging, it is apparent how inefficient packaging materials of construction, packaging design, and fabrication could limit the performance of semiconductors. Materials for packaging range from metals to ceramics to organic polymers. The use of polymers ranges from interlayer dielectrics, to passivation layers, to die attach adhesives, and to chip encapsulants (both molding and adhesive) and underfill materials, to name a few application areas. Most chips are packaged as single chips today. However, to the extent that applications requiring advanced high-density chips are more in demand, multichip packages (or modules, MCMs) are becoming preferred since they decrease the wiring distance be-

tween chips by packaging the chips as close together as possible to reduce the propagation delay and increase the packaging interconnect wiring [73].

In order to leverage the great strides made in semiconductors, focus must now turn to improvements in packaging. The four main functions of electronic packaging are: signal distribution, power distribution, heat dissipation, and protection [74]. As Shaw states: "Simply put, the package enables the chip to communicate to the outside world by connecting small bonding elements on the chip (pads or small solder balls) to a printed circuit board network" [75].

Several MCM designs have been developed: MCM-C (ceramic substrate), MCM-L (laminated substrate), MCM-Si (silicon substrate), and MCM-D (deposited dielectric substrate). For MCMs, according to Feger and Feger [76], polymers are becoming the dielectric materials of choice because:

- The low dielectric constant of polymers allows higher packaging densities, faster transmission speeds, and lower power consumption.
- Polymers are easy to process.
- Polymeric properties can be tailored by changing their chemical compositions.

This is especially true for MCM-D/L (deposited dielectric over laminated) technology. These thin film multi-layered structures have the capability of closing the gap between the feature geometries of integrated circuits (about 1 micron) and printed wiring boards (about 50–100 microns). This technology promises the ultimate in packaging, providing the highest density and speed in electronic devices.

B. F. Goodrich, along with Georgia Institute of Technology's Packaging Research Center, have been developing cyclic olefin-based Avatrel dielectric polymers that exhibit many of the key performance criteria required for this demanding application. They include:

- *Excellent, isotropic electrical properties.* Dielectric constants of 2.4 to 2.6 have been demonstrated. Low dielectric constant is crucial as interconnect density increases. As space between conducting lines shrinks, inductance and cross-talk become problematic, but can be mitigated with lower dielectric constant materials. Polyimides, which are used extensively in the industry, exhibit anisotropic electrical properties; in-plane dielectric constant can be as high as 4 while out of plane dielectric constant is generally above 3.
- *Very low moisture absorption.* Typically, Avatrel polymers absorb less than 0.1 wt.% water, while polyimides typically range from 2 to 3 wt.%. Water uptake increases the dielectric constant of the medium and can facilitate conductor corrosion.
- *Good thermo-mechanical properties.* Glass transition temperatures range from 300 to 340 °C. Thermal stability is good up to 400 °C. Elongation to break is typically 20%. On wafer stress is 18 MPa, less than half that found for typical polyimides.
- *Good adhesion to metals.* Avatrel exhibits good adhesion (passes the cross-hatched tape test, ASTM D-3359-95a and IPC 650-TM) to metals such as Cu, Au, Al, Cr, Ti, and Si, as well as SiO₂. Polyimides on the other hand require tie layers and adhesion promoters.

In the case of Goodrich poly(norbornene) dielectric polymers [77] (Avatrel) low levels (2–10 mol%) of triethoxysilylnorbornene (**I**, $R_1 = \text{H}$, $R_2 = \text{Si}(\text{OEt})_3$) are used to impart good adhesive properties, with the remaining 90+% of the monomer being an alkylnorbornene (**I**, $R_1 = \text{H}$, $R_2 = \text{alkyl}$). The alkylnorbornene is selected to tailor the glass transition temperature of the polymer (Section 4.2.3.8) and to impart toughness into the product.

A copolymer containing an 80:20 molar ratio of norbornene and 5-triethoxysilylnorbornene made using the $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$ initiator (Section 4.2.3.9) had a tensile modulus of 1.4 GPa, an elongation to break of 15% and a T_g of 355 °C. This material exhibited excellent transparency with greater than 90% average transmission between 400 and 700 nm and a low dielectric constant (2.67) suggesting that this material could find utility in optical and electronic applications [78].

An 80:20 norbornene:5-triethoxysilylnorbornene copolymer made with $[(\eta^3\text{-crotyl})\text{Ni}(\text{1,5-COD})]\text{PF}_6$ (naked nickel), while possessing similarly good optical and dielectric properties, however, gave more brittle polymers, despite being equivalent in molecular weight. These polymers were determined to have an atactic polymer architecture (i.e., 50% *m* and 50% *r*) as described in Section 4.2.3.7. Likewise, scaling behavior for the two polymers was quite different. As one examines the scaling exponent of the logarithm of intrinsic viscosity versus the logarithm of molecular weight, one finds a scaling coefficient of 0.5 for the polymer derived from the ionic nickel catalyst and a coefficient of 1 for the neutral nickel catalyst. This indicates a completely random coil behavior for the copolymer made using the ionic nickel catalyst and semi-rigid rod behavior for that obtained from the neutral nickel catalyst. Thus, it is not surprising that their mechanical properties are significantly different.

Optical Polymers

The optical polymers have a similar composition, primarily an alkylnorbornene to impart toughness and a low (typically <10%) amount of a norbornene bearing an oxygen-containing functional group (to increase chain-chain interactions, improving overall polymer properties). Potential applications for these high T_g cycloaliphatic optical polymers such as the Appear material include flat panel display substrates, optical TAB (tape automated bonding), optical wave-guides (both core and cladding) and optical data storage. In essence, Appear optical polymers would be suited for any application that requires high quality optical transmission, low birefringence, high use temperature, exceptional moisture resistance and moisture barrier properties. Much of this development was made possible by an award from the National Institute of Standards and Technology's Advanced Technology Program (ATP) [79] which supported a collaboration between B.F. Goodrich and 3M Company from 1995 until 2000.

Photoresist Polymers

The electronics revolution is due in part to the dramatic increase in information-processing capability provided by the invention of the integrated circuit (IC or

chip) in 1960. Information-processing capability is directly linked to the number of components (transistors, capacitors, and resistors) that can be manufactured on the silicon substrate. Enabling technologies for chip manufacture are, for example, thin film deposition, etching, and lithography. Lithography enables the chip designer to transfer the electronic circuitry “blueprint” that is written on a photo-mask onto the silicon wafer.

There are two types of photoresists: negative and positive photoresists. The negative resist reacts upon exposure to light to form an insoluble form of the photoresist. Addition of developer then dissolves the unexposed regions of the resist. A positive resist reacts when irradiated to produce a soluble form of the resist that is then washed away by the developer.

A typical lithographic positive photoresist process can be summarized as follows: Step 1: A photoresist is spin-coated onto a silicon wafer. Step 2: The photoresist is exposed by shining light through the photomask. Step 3: The photoresist is developed by dissolving away the unreacted photoresist. Step 4: The exposed oxide is etched away. Step 5: The remaining photoresist is stripped to give a patterned silicon wafer. While there are several types of lithography (e.g., X-ray and electron-beam), the electronics industry has invested much of its capital in UV-lithography.

The ability to pack more components on a chip is related to the feature size of the components themselves. While the 1K DRAM chip relied on feature sizes of around 10 μm , the 256 M chip has been manufactured using feature sizes of 0.35 μm , almost a two order of magnitude decrease. The industry has responded to the call for smaller feature sizes by moving to shorter and shorter wavelength UV light, from 436 nm (G-line) to 365 nm (I-line), and more recently to 248 nm light. This is because resolution (R) is directly proportional to the wavelength (λ) of the incident irradiation [80]. For G- and I-line irradiation, positive-tone novolac-diazanaphthoquinone photoresists are the industry standard.

Advances in photoresist technology have made the move to 248 nm wavelengths possible. The use of novolac-diazanaphthoquinone resists at this wavelength is limited by the system's strong UV absorbance. Poly(hydroxystyrene) (or PHS) was found to be a suitable polymer backbone around which the 248 nm photoresists could be built. PHS is marginally transparent at 248 nm. Without sufficient transparency, light cannot penetrate to the bottom of the resist film, resulting in only a partially developed resist. As wavelengths get shorter, the sources become dimmer. Efficient use of photons becomes paramount.

The use of poly(norbornene) polymers such as Duvcor in photolithographic applications is possible because of their transparency in the deep UV region (193 nm), and the ability of the nickel and palladium catalysts to polymerize norbornenes bearing a variety of functional groups. However, simply being transparent at the wavelength of interest is only the first hurdle in choosing a candidate polymer backbone. A commercial photoresist must not only undergo the appropriate solubility switch upon irradiation, but the insoluble polymer that remains after aqueous base development must “resist” decomposition under plasma etching conditions, i.e., conditions in which the exposed portions of the silicon wafer are etched away. Otherwise 3-D features, and therefore components, could not be

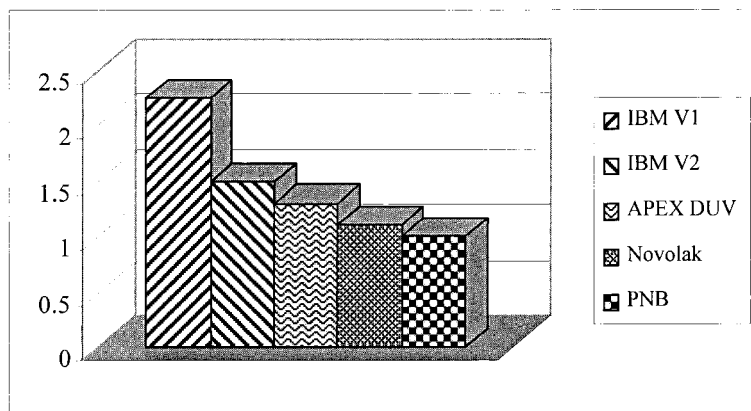


Fig. 4.32 Relative reaction ion etch rates of various photoresist polymer candidates.

built into the wafer. Thus, etch rate is a very important parameter that must be measured for candidate photoresist polymers: the lower the etch rate, the better. In Fig. 4.32, the etch rate of five polymers are presented. The two IBM samples and the APEX materials are all based on acrylate repeat units, while the novolak material is a phenolic resin used in early photoresists. The aromaticity, and hence strong UV absorbance, of the phenolic resin makes novolak impractical for deep UV applications.

All of these experimental polymers have higher etch rates than standard novolak resists (normalized to 1) except one: addition polymerized poly(norbornene). The cycloaliphatic backbone of the polynorbornenes imparts both transparency and a very low etch rate (i.e. a high reactive ion etch resistance (RIE)). Finally every monomer unit bears a functional group (typically esters, ethers and the like) to tailor key parameters such as adhesion and “wettability” (i.e. hydrophilicity), T_g , physical properties and solubility. Finally a significant portion of the functional groups (typically in the range 10–40%) represent the “solubility switch”. A chemically amplified resist system typically contains a photosensitive acid generator (or PAG) such as triarylsulfonium hexafluorophosphate and a polymer containing an acid-sensitive moiety. This moiety or “solubility switch” undergoes an acid (released by photolysis of the PAG) catalyzed deprotection forming a functionality that renders the formally solvent soluble polymer aqueous base soluble. In practice, derivatives of poly(norbornene) are protected from unexposed dissolution through a judicious choice of an acid-reactive group such as a *t*-butylcarboxylic acid ester.

Along with a photochemically activated solubility switch, UV transparency and ion etch resistance, a viable photoresist polymer must exhibit some degree of hydrophilicity. This will help in the adhesive and film forming properties of the polymer as well as the dissolution rate of the exposed resist in the developer. Other considerations include glass transition temperature and mechanical proper-

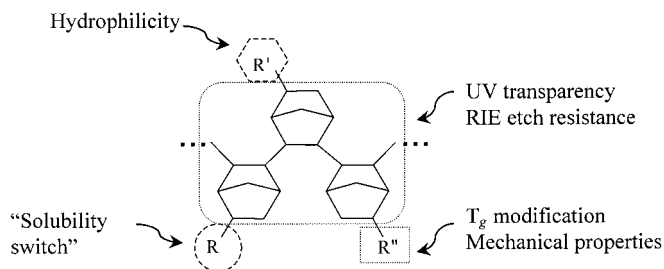


Fig. 4.33 Design of a cycloaliphatic 193 nm photoresist polymer.

ties. A balance of all of these properties is achieved by designing a polymer which has the appropriate chemical functionality, either in the polymer backbone or as a pendant group, as shown in Fig. 4.33. Functional tolerance of the B.F. Goodrich proprietary catalyst technology enables the production of cyclic olefin polymers for the demanding photoresist application.

4.3

The Copolymerization of Norbornenes with Acyclic Monomers

Early transition metal catalysts such as vanadium complexes and zirconocenes effectively copolymerize ethene with norbornene [81]. This capability eventually led to the commercial development of the APELTM and TOPASTM line of cyclic olefin copolymers by Mitsui and Ticona (formerly Hoechst), respectively [82]. Interest in this class of polymers is due to its high glass transition temperatures and transparency that is imparted by the norbornene component.

4.3.1

Copolymers with α -Olefins

Unlike early transition metals, late transition metals are more tolerant of oxygen functionalities in the monomer and the polymer. This behavior stems from the preference of late transition metals for soft ligands due to their higher electronegativity and lower oxidation states [67, 83]. The previous section reviews a number of nickel and palladium catalysts and initiators for the addition polymerization of norbornene; however, most of them are ineffective for the copolymerization of ethene/1-alkenes with norbornene because the former act as chain transfer agents through β -hydrogen abstraction. Therefore, in order to achieve the copolymerization of ethylene and 1-alkenes with functionalized norbornene, it is necessary for the catalyst to be both tolerant of functional groups and resistant to β -hydrogen abstraction.

4.3.1.1 Nickel Catalysts

In the early 1970s, patents issued detailing discoveries by Keim and co-workers at Shell regarding polymerization/oligomerization of ethene with neutral, square planar nickel complexes containing appropriate anionic, bidentate ligands, such as P–O chelates [84]. This innovation led others to broaden the scope of nickel compounds as oligomerization/polymerization catalysts [85]. It was found that catalysts of this type are not inhibited by the presence of solvents containing functional groups, and that they polymerize acyclic functional olefins [86]. Recently, there has been renewed interest in polymerization and copolymerization of ethene using nickel catalysts with chelating, anionic ligands [87].

At B.F. Goodrich we found that this type of catalyst, depicted in the generic structure in Fig. 4.34 (where E=P, As, Sb, O, or N; X=O or S; Y=saturated or unsaturated hydrocarbyl chain, L is an ancillary ligand), is effective in the copolymerization of ethylene with norbornene-type monomers (both nonfunctional and functionalized in the 5-position, R-NB) [88]. The application of these catalysts for the copolymerization of ethylene and norbornenes was first conceived and demonstrated by our collaborators Makovetsky and Finkelshtein at the Topchiev Institute of Petrochemical Synthesis in Moscow.

Fig. 4.35 shows the structures of typical nickel compounds of this family. They all contain a Ni-Ph moiety and the same P–O chelate ligand. They only differ in terms of their donor ligand, L. Compounds **8**, **10**, **11**, and **12** are bonded to L=pyridine, $\text{Ph}_3\text{P}=\text{CH}_2$, PPh_3 , and $\text{O}=\text{PPh}_3$, respectively. Compound **9** differs somewhat in that it is dimeric and is held together by virtue of donor interactions with the oxygen atom of the P–O chelate.

Effect of Ethylene Pressure

Increasing the ethylene pressure has a significant influence on the polymerization reaction. As the ethylene pressure is raised from 50 to 300 psig, the conversion of norbornene increases until nearly complete consumption is achieved. Accordingly, the catalyst activity also increases by more than an order of magnitude. Increasing the ethylene pressure also significantly raises the incorporation of ethylene in the copolymer, with the molar ratio of ethylene to norbornene in the copolymer rising from 1:1 to 3:1. At the same time, the molecular weight is cut almost in half, from 74 000 to 40 000. Up to 50 mol% incorporation of norbornene, leading to an essentially alternating copolymer, is obtained. Higher incorporation does not occur because of steric congestion resulting from the coordination of norbornene to the catalyst center with a nickel-norbornyl linkage.

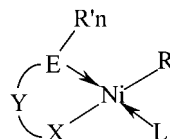


Fig. 4.34 Generic formula of neutral nickel catalysts used in the copolymerization of norbornene and ethylene.

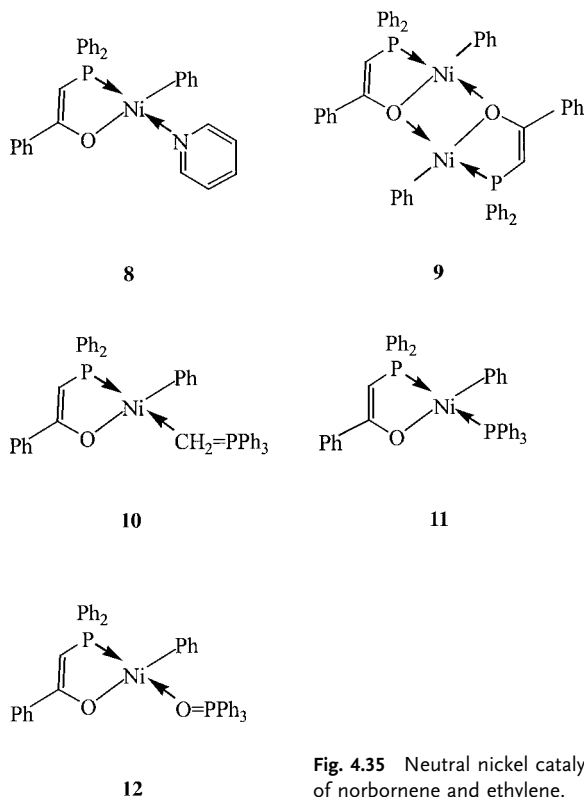


Fig. 4.35 Neutral nickel catalysts used in the copolymerization of norbornene and ethylene.

Finally, the ethylene/norbornene copolymers obtained using the nickel catalysts are essentially indistinguishable from those obtained using metallocene-based early transition metal catalysts, both in terms of the microstructure and such physical properties as T_g and tensile modulus. For the ethylene/norbornene polymers synthesized, the glass transition temperature (T_g) increases smoothly with increasing norbornene content.

Functionalized Norbornenes

A distinct advantage of the nickel catalysts, when compared to the corresponding early transition metal-based analogs (metallocenes and the like), is their ability to copolymerize norbornene derivatives bearing oxygen functionalities. However, compared to norbornene itself the level of incorporation of these functionalized norbornenes is lower, as are the reaction rates and polymer molecular weights. Also, substantially higher amounts of catalyst are required to copolymerize functionalized norbornenes.

For all the functionalized norbornenes tested, the level of incorporation in the copolymer with ethylene was substantially lower than that for the norbornene it-

self under similar conditions. The catalytic activity was also sharply attenuated with functional norbornenes.

Terpolymerizations

These nickel-based compounds with P–O ligands also proved to be capable of terpolymerizing norbornenes and ethylene with 1-alkenes. As in copolymerizations with ethylene, the level of incorporation of 5-*n*-butylnorbornene in the terpolymers was lower than that of norbornene. Additionally, the molecular weights obtained were lower, suggesting that the incorporation of the 1-alkene facilitates chain termination.

4.3.1.2 Palladium Catalysts

The nickel catalysts described in the preceding section are neutral in character, in our hands cationic nickel catalysts such as those described by Brookhart et al. [20] are ineffective in the copolymerization of norbornene and ethylene. Indeed norbornene has been described as a strong catalyst poison (for both nickel and palladium) by the same workers. Surprisingly we found that cationic palladium catalysts, with a wide variety of chelate ligands, are very effective in the copolymerization of ethylene and norbornenes [89]. These catalysts possess the same ability as the above-described neutral nickel catalysts to incorporate norbornenes bearing functional groups, but overcome two of the major limitations:

- The palladium catalysts are capable of generating very high molecular weight copolymers (up to >800 000; more than an order of magnitude higher than the capability of the nickel catalysts).
- The palladium catalysts can incorporate high levels of norbornenes (up to >90 mol% compared to the upper limit of 50 mol% achievable with the nickel systems) resulting in T_g s of in excess of 200 °C compared to a maximum of around about 130 °C in the case of nickel-generated copolymers.

The cationic palladium catalysts are typically prepared by reacting (cyclooctadiene)palladium methyl chloride with a stoichiometric amount of the bidentate ligand to afford the (ligand)Pd(Me)Cl adduct. The adduct is then reacted with an activator such as silver hexafluoroantimonate, to afford the final cationic catalyst, (ligand)Pd(Me)⁺SbF₆[−]. The polymerization reactions were typically run at ambient temperature in toluene to afford a viscous solution of the desired copolymer. Other activators used include tris(pentafluorophenyl)borane/triethylaluminum mixtures, NaB(C₆H₃(CF₃)₂)₄ and methaluminoxane.

Using simple chelating phosphines such as bis(diphenylphosphino)ethane as ligand resulted in high conversions to low molecular weight copolymers (M_w up to around 10 000) with high norbornene incorporation (up to around 65 mol%). The catalysts were also capable of incorporating norbornenes bearing alkyl substituents such as 5-butylnorbornene and functional substituents such as 5-triethoxysilylnorbornene. More useful, high molecular weight copolymers (M_w up to around

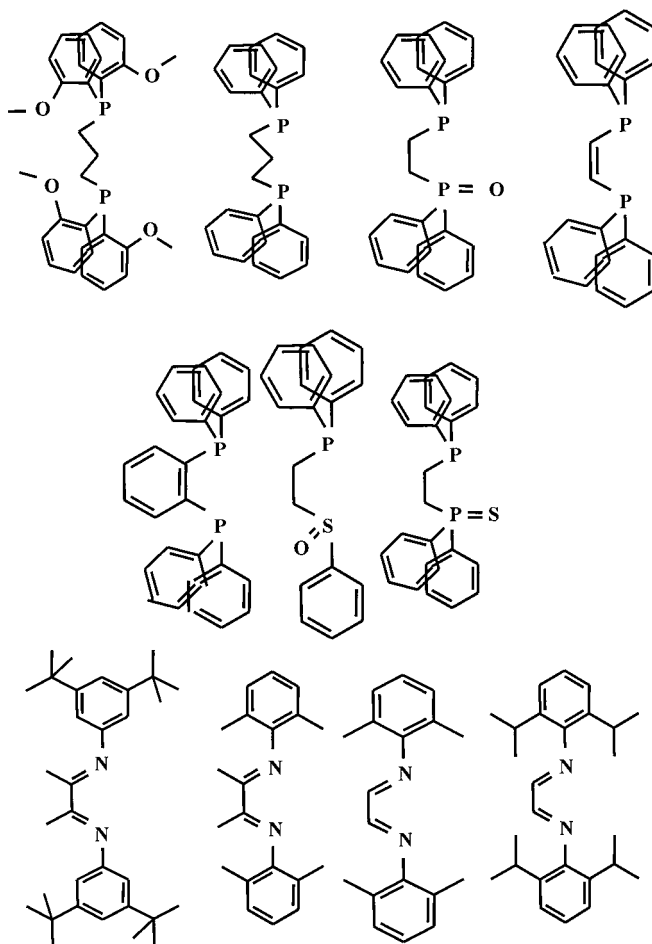


Fig. 4.36 Ligands used in the palladium-catalyzed copolymerization of ethylene with norbornenes.

800000) resulted when appropriately substituted diimine ligands were employed. The scope of the ligands exemplified [89] is illustrated in Fig. 4.36.

The structure of the di-imine ligand has a dramatic effect on the structure and properties of the copolymer formed. Firstly the phenyl rings must bear ortho-substituents in order to generate higher molecular weight polymer, just as in the case of the ethylene polymerization systems [20]. However, the presence or absence of substituents on the bridge or backbone of the ligand is absolutely critical in determining the level of norbornene that can be incorporated. This is illustrated in Fig. 4.37 where it can be seen that introducing methyl groups on to the backbone (on an otherwise identical ligand) lowers the norbornene incorporation from around 85 mol% to around 45 mol% with a simultaneous drop in T_g from around

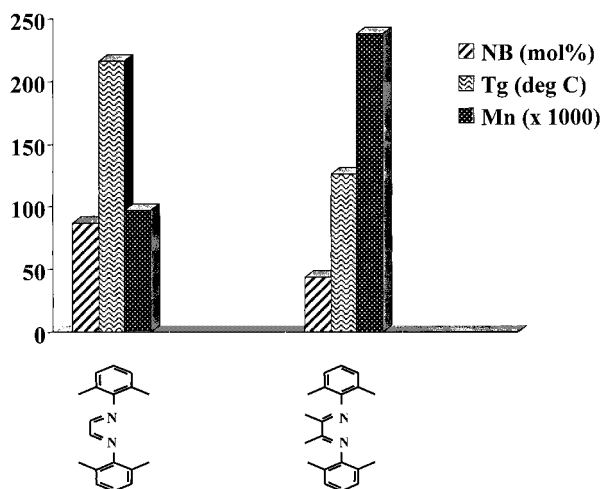


Fig. 4.37 Effect of di-imine ligand structure on copolymer properties.

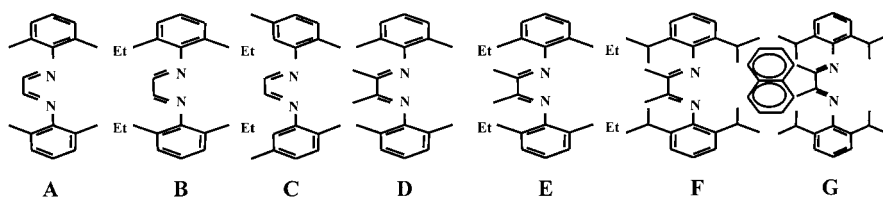
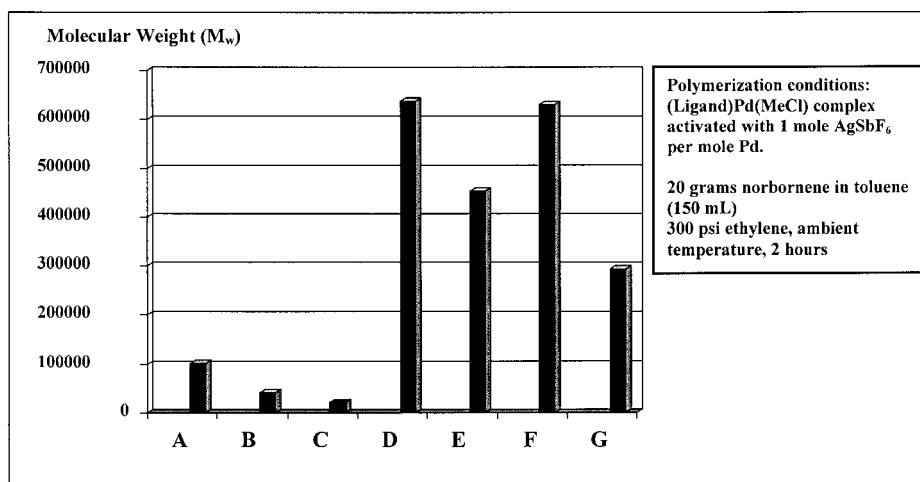


Fig. 4.38 Effect of ligand choice on copolymer M_w .

220 °C to around 130 °C. On the other hand the molecular weight increases substantially.

Fig. 4.38 shows a wider variety of di-imine ligands exemplified in the Goodrich patent [89]. Exactly the same trends are seen in terms of polymer properties; in this figure the effect of ligand backbone substitution on molecular weight is displayed. Again, no substitution on the backbone (A–C) gives low molecular weight while any substituent (D–G) results in a dramatic increase in M_w .

Our rationale for the influence of backbone substitution on the copolymerization process is that the catalyst center is extremely sterically-hindered because of the size of the growing polymer chain (with large bicyclic norbornanes incorporated) and the norbornene monomers about to insert in the growing chain. When there is no substituent on the backbone, the phenyl ring (with its ortho-substituent) can twist around to accommodate an incoming norbornene unit even when the last inserted monomer unit was a norbornene also. Therefore in this case norbornene-norbornene linkages can be formed and high norbornene content (up to >90%) can be attained with corresponding high T_g . However, the ability to rotate also permits chain transfer and results in lower molecular weights. The introduction of any substituent prevents free rotation and therefore a norbornene unit can only be accommodated after ethylene insertion, resulting in a limit of 50% norbornene incorporation (alternating copolymer) and therefore T_g .

4.4

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5

Well-Defined Transition Metal Catalysts for Metathesis Polymerization

MICHAEL R. BUCHMEISER

5.1

Introduction

Quite late on (that is in the 1980s), metathesis polymerization has been added to the armour of transition metal-catalyzed polymerizations. The mechanism of ring-opening metathesis polymerization (ROMP) was elucidated by Dall'Asta et al. who provided unambiguous evidence for the total cleavage of the double bond of the starting monomer during polymerization [1]. The originally proposed mechanism that suggested the existence of a metal carbene [2] was further supported by the work of Katz et al. [3, 4]. Consecutive investigations mainly carried out by the leading groups of Schrock et al. [5–7], Grubbs et al. [8–12] and Feast et al. [13–23] initiated further research on that area [24]. The enormous potential of metathesis-based polymerizations such as ROMP, acyclic diene metathesis polymerization (ADMET polymerization), and alkyne polymerization in materials science was soon recognized. In due course, enormous effort has been put into the development of new, more efficient and selective catalytic systems, resulting in an impressive variety of catalytic systems based on Ti, V, Nb, Ta, Cr, Mo, W, Re, Co, Rh, Ir, Ru and Os [25–27].

This chapter will cover both the synthesis and basic principles of modern, *well-defined* metal alkylidenes related to their use in ROMP, ADMET-polymerization and alkyne metathesis polymerization. The term “well-defined” is limited to catalytic systems, usually metal alkylidenes, that are characterized by a *uniform* and *stoichiometric* composition and for which the actual propagating species is well known and characterized. Consequently, the entire chemistry of standard binary or ternary systems such as $\text{WCl}_6/\text{AlEt}_2\text{Cl}$ /ethanol has been neglected. Where applicable, general aspects of the preparation of advanced materials via ROMP and alkyne-polymerization will be mentioned briefly.

5.2

Transition Metal Alkylidenes [28]

5.2.1

Group IVA and VA Transition Metal-Based Initiators

Though this book focuses on late transition metals, the few well-defined Group IVA- or VA-based systems that exist shall be outlined briefly. Among the first transition metal alkylidenes that were observed in ROMP was the bimetallic compound ($\text{Cp}_2\text{TiCH}_2\text{ClAlMe}_2$) [29, 30]. Upon reaction with norborn-2-ene (bicyclo[2.2.1] hept-2-ene, NBE) at ambient temperature it forms the metallacycle shown in Fig. 5.1 which opens at 65 °C under ring-opening [31].

This system was the first well-documented example of a truly “living” [32–36] ROMP. In analogy, Cp_2TiMe_2 , Cp_2TiMe_3 , $\text{Cp}_2\text{TiMe}_2\text{Cl}$, and $\text{Cp}_2\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$ catalyze the ROMP of NBE. The rate-determining step was proposed to be the loss of CH_4 , ClCH_3 , and SiMe_4 , respectively [37]. Other Ti-alkylidenes exist, yet are not of any significance to polymer chemistry [38].

Nb and Ta form a number of well defined and stable metal carbenes such as $\text{Cl}_2\text{CpTa}(\text{=CHCMe}_3)$ and $\text{Cl}_2\text{CpTa}(\text{=CHCMe}_3)\text{PMe}_3$ [6, 39, 40]. In particular $\text{Ta}(\text{=CHCMe}_3)(\text{O}-2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3)_3(\text{THF})$ and $\text{Ta}(\text{=CHCMe}_3)(\text{TIPT})_3$ (TIPT = 2,4,6-*i*-Pr₃-C₆H₂-S-) are good initiators for living ROMP [41, 42]. $\text{Ta}[\text{CMeCMeCHCMe}_3](\text{DIPP})_3$ (DIPP = 2,6-*i*-Pr₂-C₆H₄-O), Fig. 5.2) has been reported to allow the living polymerization of 2-butyne up to a degree of polymerization (DP) of 200 [43]. So

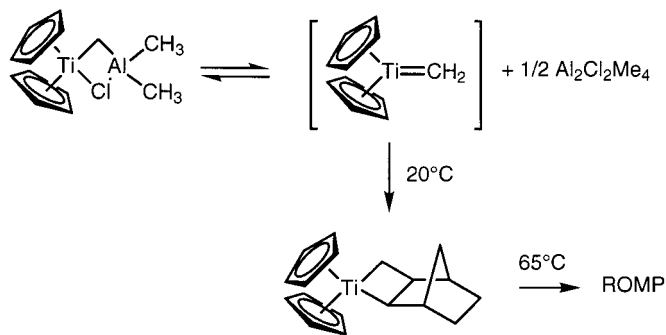


Fig. 5.1 Reaction of NBE with $\text{Cp}_2\text{TiCH}_2\text{ClAl}(\text{CH}_3)_2$.

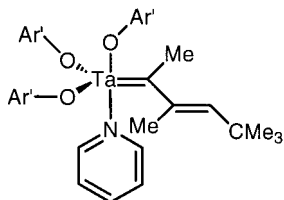


Fig. 5.2 Structure of $\text{Ta}[\text{CMeCMeCHCMe}_3](\text{DIPP})_3$ ($\text{Ar}' = 2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3$).

far this is the *only* well-defined catalyst-monomer combination involving *internal* alkynes that represents a polymerization-active system.

5.2.2

Group VI Transition Metal-Based Initiators

5.2.2.1 Chromium-Based Initiators

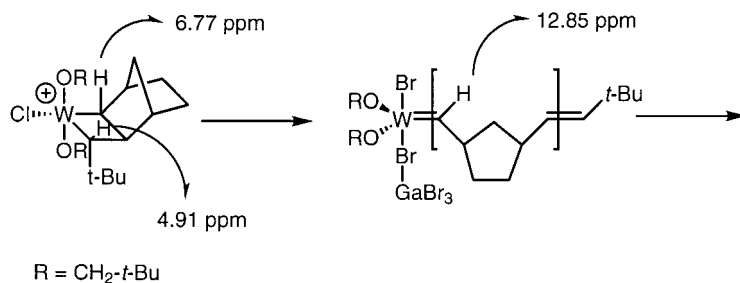
Only few reports exist on the successful use of chromium carbenes for ROMP. These few examples comprise the ROMP of 2,3-dihydrofuran catalyzed by $\text{Cr}(\text{=CPh}_2)(\text{CO})_5$ [44] as well as the ROMP of 2,3,4,5-tetrahydrooxypin-2-yl acetate [45].

5.2.2.2 Tungsten-Based Initiators

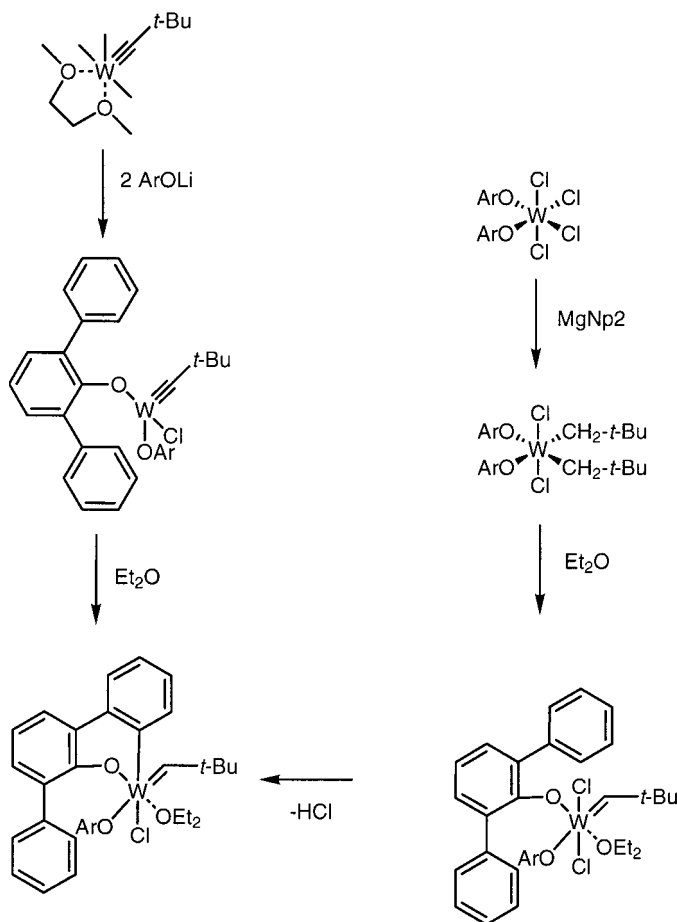
Tungsten-alkoxy-alkylidene Complexes

Following the reports of Casey et al. on tungsten(0) complexes [46, 47], the first well-defined high oxidation state tungsten(VI) alkylidenes, $\text{W}(\text{=CR}_2)(\text{OCH}_2\text{-}t\text{-Bu})_2\text{X}_2$ and $\text{W}(\text{=CR}_2)(\text{OCH}_2\text{-}t\text{-Bu})_3\text{X}$ ($\text{X}=\text{Cl, Br, I}$; $\text{R}=\textit{n}$ -Bu, *sec*-Bu, *t*-Bu, Ph, *a,ω*-cyclopentadienyl) were reported by J.A. Osborn and co-workers [48, 49]. Upon addition of GaBr_3 , $\text{W}(\text{=CH-}t\text{-Bu})(\text{OCH}_2\text{-}t\text{-Bu})_2\text{Cl}_2$ polymerizes a variety of substituted NBEs. Using this compound, the living character of such a tungsten(VI)-based polymerization system was observed for the first time via $^1\text{H-NMR}$ spectroscopy [50] and further supported by the successful synthesis of *block*-copolymers. Additionally, by employing low-temperature techniques, an intermediate (cationic) tungsta-cyclobutane species [51] was observed (Scheme 5.1) [52–55]. In a consecutive study, the equilibria that are relevant for ROMP have been studied in detail [56].

One of the first examples of Lewis-acid free initiators based on tungsten(VI), $\text{W}(\text{O-2,6-}i\text{-Pr}_2\text{-C}_6\text{H}_3)_2\text{Cl}_2(\text{CH-}t\text{-Bu})(\text{OR})_2$, ($\text{R}=\text{Et, } i\text{-Pr}$), which allowed the polymerization of substituted NBEs, was reported by J.M. Basset et al. [57]. Additionally, Lewis-acid free $\text{W}(\text{=C}(\text{CH}_2)_4)(\text{OCH}_2\text{-}t\text{-Bu})_2\text{Cl}_2$ was reported to effectively polymerize substituted NBEs such as *exo*-norborn-5-ene-2,3-dicarboxylic anhydride [58, 59].



Scheme 5.1 Observation of the simultaneous presence of metal alkylidenes and metallacyclobutanes via $^1\text{H-NMR}$ spectroscopy.



Scheme 5.2 Synthesis of a ROMP-active cyclometallated aryloxy(chloro)neopentylidene tungsten complex [60].

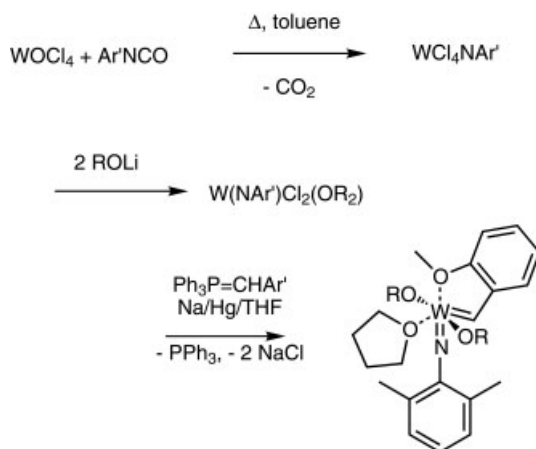
Finally, the synthesis of the aryloxy(chloro)tungsten alkylidene complex reported by Basset et al. needs to be mentioned (Scheme 5.2) [60].

The synthesis may be accomplished via two independent routes. One entails the reaction of $\text{W}(\text{C}-t\text{-Bu})\text{Cl}_3 \cdot \text{DME}$ ($\text{DME} = 1,2\text{-dimethoxyethane}$) with 2 equiv. of $\text{Ar}'\text{OLi}$ ($\text{Ar}' = 2,6\text{-(C}_6\text{H}_5)_2\text{-C}_6\text{H}_3$). The intermediary alkylidyne is believed to spontaneously isomerize to the desired alkylidene moiety. Alternatively, $\text{WCl}_4(\text{OAr})_2$ is reacted with 2 equiv. of dineopentyl magnesium (Np_2Mg). Elimination of neopentane and HCl again results in the formation of desired catalyst. It has been reported to be highly active and stereoselective in the ROMP of 1-methylnorbornene to yield predominantly *cis*-polymers on a strong head to tail base [61].

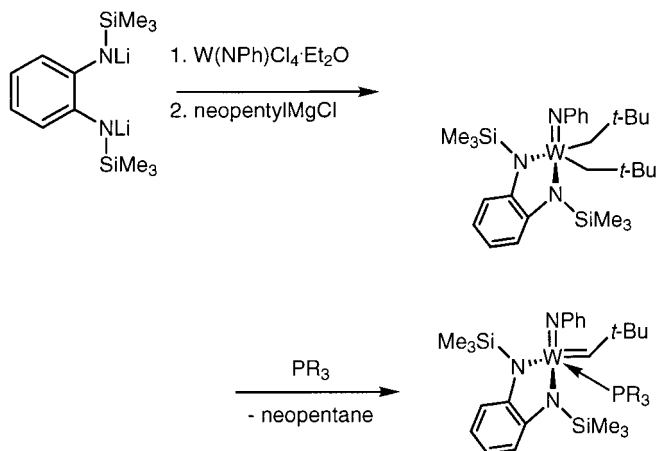
Tungsten-imido-alkoxy-alkylidene Complexes

The first living polymerization of other cyclic strained olefins than NBE [62] such as substituted NBEs, norbornadienes (bicyclo[2.2.1]hepta-2,5-dienes, NBDEs) or the “FEAST-monomer” 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDTF6) by $W(N-2,6-i-Pr_2-C_6H_3)(CH-t-Bu)(OCMe(CF_3)_2)$ [63] was reported in 1987 [64]. The initiator may conveniently be prepared either by reaction of $W(NAr')(O-t-Bu)_2(CH_2-t-Bu)_2$ with PCl_5 [65] or via base-catalyzed reaction of $W(C-t-Bu)Cl_3$ with $N(TMS)H-2,6-i-Pr_2-C_6H_3$ (TMS=trimethylsilyl) [66]. Isolable metallacyclobutanes were reported to result from the reaction of this compound with ethylene, *t*-butylethylene [67], methyl acrylate and *N,N*-dimethylacrylamide [68]. The synthesis of W-alkylidenes of the general formula $W(CH-t-Bu)(NAr')(OTf)_2$ ($OTf=CF_3-SO_3$, triflate) was first described in 1990 by Schrock and co-workers [69] and later adapted for the synthesis of the corresponding analogous molybdenum compounds. Similar tungsten-based systems were elaborated by Grubbs and co-workers [70]. Starting from $WOCl_4$, addition of an aryl isocyanate followed by thermal treatment leads to the formation of a tungsten arylimidotetrachloride. Reaction with 2 equiv. of an alkoxide followed by reduction in the presence of a phosphorane yielded the desired complex (Scheme 5.3).

Van der Schaaf reported on the photoinduced ROMP of NBE and dicyclopentadiene (DCPD) using $W(NPh)(OCMe(CF_3)_2)_2(CH_2SiMe_3)_2$ and $W(NPh)Cl(CH_2SiMe_3)_3$, respectively, as tungsten alkylidene precursors [71]. Unfortunately, the corresponding ROMP-active species were not isolated. Nevertheless, their existence was indirectly proven by reaction with an aldehyde and characterization of the resulting alkene. A diamido tungsten(VI)-based catalyst was reported by Boncella and co-workers [72]. It was prepared from the dilithio salt of *N,N'*-bistrimethylsilyl-protected *o*-phenylenediamine and $W(NPh)Cl_4(OEt_2)$. The conversion of the intermediate bisalkyl complex into the corresponding tungsten alkylidene requires the addition of an ex-



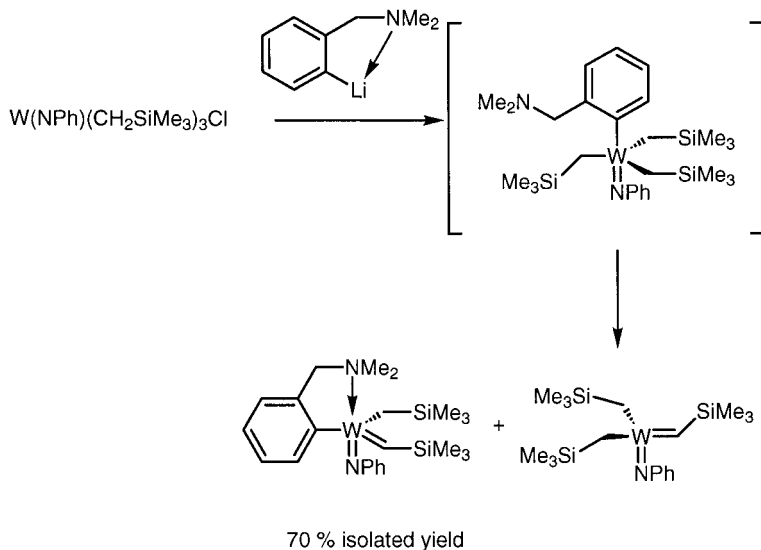
Scheme 5.3 Synthesis of a tungsten alkoxyimidoalkylidene complex by alkylidene transfer from a phosphorane to a tungsten imide.



Scheme 5.4 Preparation of $W(NPh)(CHCMe_3)(TMS_2PDA)L$ ($L = PMe_3$). PDA = *o*-phenylene diamide.

cess of base such as trimethylphosphine or triethylphosphine at elevated temperatures (Scheme 5.4).

$W(NPh)(CHCMe_3)(TMS_2PDA)L$ (PDA = *o*-phenylenediamide, $L = PMe_3$) also effectively catalyzes the polymerization of NBE. Unfortunately, a non-stoichiometric initiation due to incomplete dissociation of the base was observed. Another tungsten-based complex $W(NPh)(CHSiMe_3)(CH_2SiMe_3)(2-NMe_2-CH_2C_6H_4)$ may be prepared

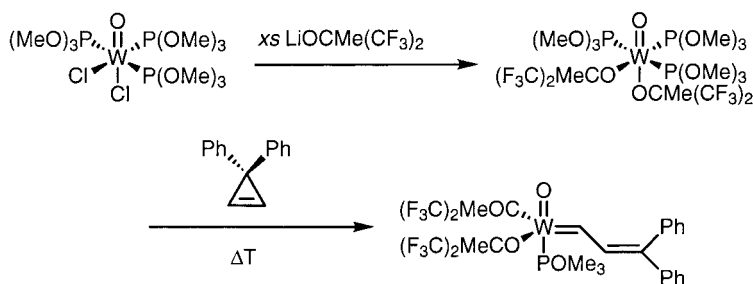


Scheme 5.5 Synthesis of $W(NPh)(CHSiMe_3)(CH_2SiMe_3)(2-NMe_2-CH_2C_6H_4)$.

via the synthetic protocol shown in Scheme 5.5 [73]. It was reported stable up to $T=80^{\circ}\text{C}$ and turned out to be an efficient initiator for the polymerization of NBE yielding poly-NBE with a *cis*-content of $>90\%$.

Tungsten-oxo-alkoxy-alkylidene Complexes

A tungsten-oxo-alkylidene, $\text{W}(\text{O})\text{CHCHCPh}_2(\text{OCMe}(\text{CF}_3)_2)_2 \cdot \text{P}(\text{OMe}_3)$, and its analogue $\text{W}(\text{O})\text{CHCHCPh}_2(\text{OCMe}(\text{CF}_3)_2)_2 \cdot \text{THF}$ were reported to be active in the ROMP of NBE [74]. The synthetic route to these initiators entails the reaction of $\text{W}(\text{O})\text{Cl}_2[\text{P}(\text{OMe}_3)_3]$ with $\text{LiOCMe}(\text{CF}_3)_2$ and 2,2-diphenylcyclopropene (Scheme 5.6).



Scheme 5.6 Synthesis of $\text{W}(\text{O})\text{CHCHCPh}_2(\text{OCMe}(\text{CF}_3)_2)_2 \cdot \text{L}$ ($\text{L} = \text{P}(\text{OMe}_3)$, THF).

This reaction of 2,2-diphenylcyclopropene with a transition metal complex has also been used for the synthesis of Ru-based alkylidenes [75]. Another ROMP-active tungsten-oxo-complex, $\text{W}(\text{CH-}i\text{-Bu})(\text{O})(\text{PMe}_3)_2(\text{OAr})_2$, was obtained by reaction of $\text{W}(\text{CH-}i\text{-Bu})(\text{O})(\text{PMe}_3)_2\text{Cl}_2$ with $\text{KO-2,6-Ph}_2\text{-C}_6\text{H}_3$ [76]. This complex was reported to be active in the ROMP of 2,3-bis(trifluoromethyl)-NBD and 2,3-dicarbomethoxy-NBD, producing highly tactic ($>95\%$) polymers with a high *cis*-contents ($>95\%$). Finally, Boncella and co-workers reported on the use of the tris(3,5-dimethyl-1-pyrazolyl)borate (Tp') ligand for the preparation of the tungsten oxoalkylidene complex $\text{W}(\text{O})(\text{CH-}i\text{-Bu})(\text{Cl})(\text{Tp}')$ which was found to be an active ROMP catalyst for cyclooctadiene (COD) in the presence of aluminum chloride [77].

5.2.2.3 Molybdenum-Based Initiators

Molybdenum-imido-alkoxy-alkylidene Complexes

In view of the more than encouraging results obtained in ROMP with W-based initiators, the development of the analogous Mo compounds was pushed forward. This development was mainly driven by two general aspects of organomolybdenum chemistry. On one hand, the analogous molybdenum complexes could be prepared in a more convenient way in terms of starting compounds and stability compared to the parent W systems. On the other hand, the corresponding Mo initiators turned out to be even more functionality tolerant than the corresponding tungsten systems [78–80]. Thus, functional monomers containing olefins, ethers,

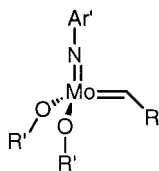
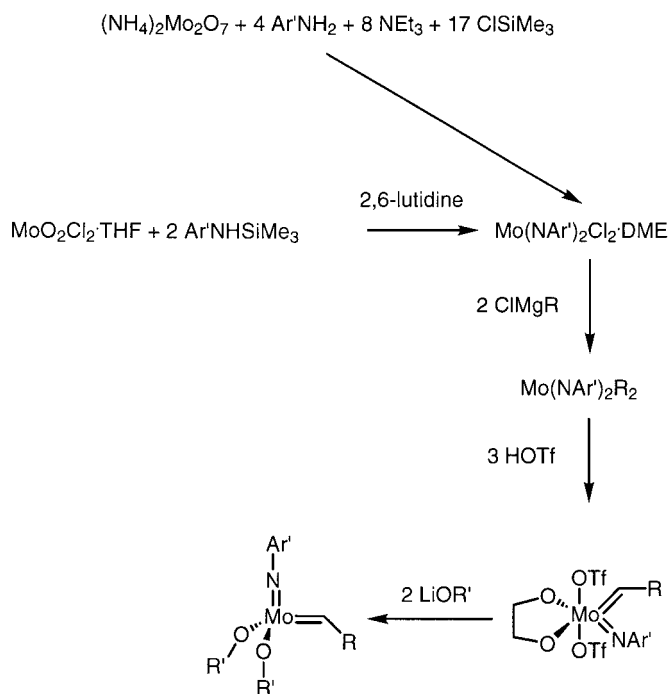


Fig. 5.3 Mo-based Schrock-type catalyst. Ar' = phenyl, 2,6-Me₂-C₆H₃, 2,6-i-Pr₂-C₆H₃, etc.; R = ethyl, phenyl, trimethylsilyl, CMe₂Ph or *t*-butyl and R' = CMe₃, CMe₂CF₃, CMe(CF₃)₂, C(CF₃)₂, aryl, etc.

esters, amides, *t*-amines, nitriles, ketones, phosphines and pyridines(!) can be polymerized by Mo-based initiators. In 1990, Schrock and co-workers reported the synthesis of these well-defined high-oxidation state molybdenum alkylidenes [81]. These and the analogous tungsten systems are now commonly named “Schrock-catalysts”. The systems possess the general formula $M(NAr')(CHR)(OR')_2 \cdot L$, where $M = Mo, W$, $Ar' =$ phenyl or a substituted phenyl group, $R =$ ethyl, phenyl, trimethylsilyl, CMe₂Ph or *t*-butyl and $R' =$ CMe₃, CMe₂CF₃, CMe(CF₃)₂, C(CF₃)₂, aryl, etc. (Fig. 5.3).

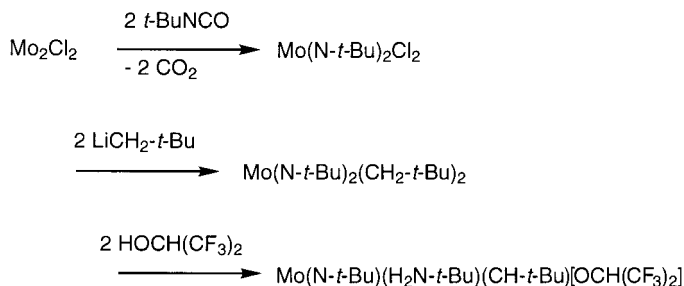
Commonly used and also commercially available systems are based on the neophylidene, the 2,6-*i*-Pr₂-C₆H₃-imido and the *t*-butoxide, hexafluoro-*t*-butoxide and various chiral binaphtholate ligands. The synthesis of Mo-based compounds initially started from Mo(C-*t*-Bu)Cl₃ · DME which was reacted with 1 equiv. of TMS-SiNHAr' to form Mo(C-*t*-Bu)(NHAr')Cl₂ · D [82]. This compound was transformed into Mo(CH-*t*-Bu)(NHAr')Cl₂ · DME by reaction with 0.25 equiv. of triethylamine. Owing to the synthetic restrictions related to the formation of Mo(CH-*t*-Bu)(NHAr')Cl₂ · DME, an alternative route starting from MoO₂Cl₂ · 2THF was elaborated. Reaction of this compound with 2 equiv. of TMS-NHAr' in the presence of an auxiliary base, such as 2,6-lutidine, in DME resulted in the formation of Mo(NAr')₂Cl₂ · DME. Even more convenient, the formation of Mo(NAr')₂Cl₂ · DME was later accomplished starting from various ammonium molybdates [83] or sodium molybdate [84]. While a large variety of arylamines may be used, the use of the corresponding alkyl-analogue is more or less restricted to sterically demanding amines such as *t*-butyl amine.

Similar bisimido complexes of the general formula Mo(NAr')₂Cl₂ · THF were reported by Osborn and co-workers [85]. They prepared molybdenum bis(2,6-di-*i*-propylphenylimido)dichloride · THF by reaction of freshly sublimed MoO₂Cl₂ with 2,6-di-*i*-propylphenylisocyanate in THF at 70 °C. Molybdenum bisimido dichlorides of the general formula Mo(NAr')₂Cl₂ · DME smoothly react with Grignard reagents such as neophyl- or neopentylmagnesium chloride to yield the corresponding molybdenum bisimidoalkyl complexes. Consecutive reaction with 3 equiv. of triflic acid (HOTf) in DME yields the molybdenum(imidoalkylidene) bistriflates, which are conveniently transformed into a large variety of different Schrock-type catalysts by reaction with 2 equiv. of a lithium alkoxide [86]. A broad variety of alkoxides such as *t*-butoxide, trifluoro-*t*-butoxide, hexafluoro-*t*-butoxide, perfluoro-*t*-butoxide, phenoxides, etc. may be used for these purposes. A summary of the entire reaction scheme is given in Scheme 5.7.



Scheme 5.7 Synthesis of Mo-based Schrock-catalysts. Ar' = phenyl, 2,6-Me₂-C₆H₃, 2,6-i-Pr₂-C₆H₃, etc.; R = ethyl, phenyl, trimethylsilyl, CMe₂Ph or *t*-butyl and R' = CMe₃, CMe₂CF₃, CMe(CF₃)₂, C(CF₃)₂, aryl, etc. Tf = triflate (OSO₂CF₃)₂.

The key intermediate of the general formula Mo(NAr')(CHCMe₂R)(OTf)₂ · DME possess a pseudooctahedral conformation with the imido- and alkylidene ligand in a *cis*- and the two triflate groups in a *trans*-position. The final catalysts of the type Mo(NAr')(CHCMe₂R)(OR')₂ possess a tetrahedral geometry. More recently, even silsesquioxanes have been reported as ligands [87]. It is worth noting, that such a ligand exchange may also be performed in the course of the polymerization. Thus, after starting the polymerization of 2,3-bis(trifluoromethyl)norborn-5-ene with Mo(NAr')(CHR)(OCMe₃)₂, addition of HOCMe(CF₃)₂ leads to an alkoxide-exchange and forms a living polymer containing the Mo(NAr')(CHR)[OCMe(CF₃)₂]₂ moiety at the chain end. This approach offers access to *block*-copolymers with different *cis-trans*-configurations for the resulting double bonds [88]. Generally speaking, tungsten and in particular molybdenum Schrock carbenes are highly reactive initiators for the ROMP of a vast variety of cyclic alkenes such as substituted NBEs, NBDEs, 7-oxanorbornenes, cyclooctatetraenes (COTs), cyclooctadienes (CODs), etc. and polycyclic alkenes such as quadricyclanes [89]. Despite their sensitivity towards traces of oxygen or moisture, these systems nowadays hold a strong place due to their stability versus functional groups as well as the ease of catalyst tuning.



Scheme 5.8 Synthesis of molybdenum alkylidenes as elaborated by Osborn et al.

An alternative route to *N*-*t*-butylimido-Mo-based systems of the type $\text{Mo(N-}t\text{-Bu)}(\text{CH-}t\text{-Bu})[\text{OCH(CF}_3)_2]_2$ was reported by Osborn [90]. Starting from MoO_2Cl_2 , $\text{Mo(N-}t\text{-Bu)}_2\text{Cl}_2$ was prepared by reaction with 2 equiv. of *t*-BuNCO. Subsequent reaction with 2 equiv. of $\text{LiCH}_2\text{-}t\text{Bu}$ yields $\text{Mo(N-}t\text{-Bu)}_2(\text{CH}_2\text{-}t\text{Bu})_2$. Addition of hexafluoro-*i*-propanol yields $\text{Mo(N-}t\text{-Bu)}(\text{NH}_2\text{-}t\text{Bu})(\text{CH-}t\text{Bu})[\text{OCH(CF}_3)_2]_2$. The release of *t*-butylamine may be induced by adding acetonitrile, which replaces the amine as a ligand. Interestingly enough, this reaction may only be accomplished with hexafluoro-*i*-propanol (Scheme 5.8).

Other, less acidic alcohols show no reaction, while phenol derivatives result in the formation of dineopentyl derivatives. Finally, binuclear molybdenum alkylidenes are obtained by reaction of a Schrock carbene with α,ω -dienes such as divinylbenzene or with octatetraene [91].

Reactivity of Molybdenum-imido-alkoxy-alkylidene Complexes [92]

Addition of phosphines such as PMe_3 or amines such as quinuclidine to $\text{Mo(NAr)}(\text{CH-}t\text{-Bu})[\text{OCMe(CF}_3)_2]_2$ allows in analogy to W-based systems [66] the observation and isolation of two isomeric adducts [93]. The attack of the ligand preferably occurs at the CNO-face, a fact which is in accordance with calculations carried out for the attack of an alkene to such systems [94]. One isomer, in which the *t*-butyl or neophyl group points towards the imido-ligand is commonly called the *syn*-rotamer, the second with the *t*-butyl or neophyl group pointing away from the imido ligand is called the *anti*-rotamer (Fig. 5.4).

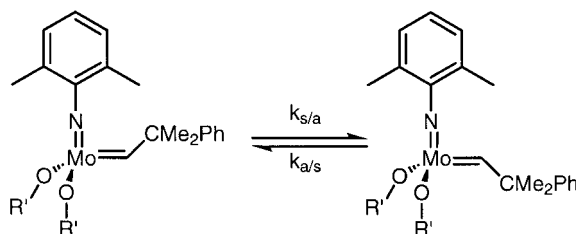
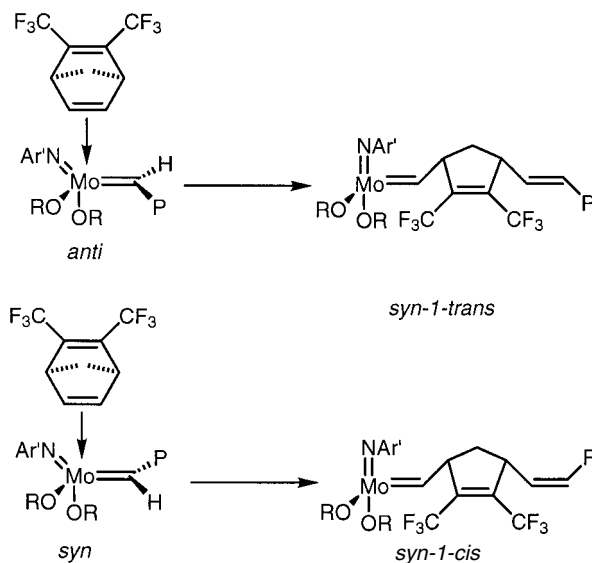


Fig. 5.4 *Syn-anti* interconversion in Mo-based Schrock carbenes.
 $\text{R}' = \text{CMe}_3, \text{CMe}_2\text{CF}_3, \text{CMe(CF}_3)_2, \text{C(CF}_3)_2$, etc.

These two rotamers, whose reactivity and relative ratio is governed by the electronic nature of the alkoxide ligand, were found to be responsible for the structure of the final polymer if used in ROMP. In-depth investigations on the reactivity of these rotamers were carried out in order to shed some light onto the mechanism that is responsible for the formation of polymers with high *cis*- or *trans*-vinylene contents. Upon photolysis of a large variety of Mo-based Schrock carbenes in different coordinating and non-coordinating solvents (toluene, THF), photostationary *syn-anti* mixtures containing up to 35% of the *anti*-rotamer were obtained [95]. Taking advantage of the different chemical shifts of the H_α -alkylidene resonances in both isomers (characterized by α -agonistic interactions with the Mo-core and typically found between 11 and 13 ppm), the first-order rates of conversion of the *anti*-rotamer into the *syn*-rotamer were determined by ^1H -NMR spectroscopy. These investigations revealed that the rate of interconversion strongly depends on the alkoxide. Thus, $k_{a/s}$ is 10^8 times higher in $\text{Mo}(\text{NAr})(\text{CHR})(\text{OR})_2$ if $\text{R} = t\text{-butoxide}$ than in the case where $\text{R} = \text{CMe}(\text{CF}_3)_2$. A comparison of these data obtained in toluene with those obtained in THF revealed a decrease for both $k_{a/s}$ and $k_{s/a}$ which was even more pronounced in the case of more electron withdrawing alkoxides such as $\text{OCMe}(\text{CF}_3)_2$. These findings were consistent with the expected stronger binding of THF by a more electrophilic metal core along with the fact that a coordinating ligand must be lost from a five-coordinate species in order to allow interconversion [93]. SCF-Xa-SW calculations were carried out on simplified analogues $\text{Mo}(\text{NH})(\text{CH}_2)(\text{OH})_2$ and confirmed the contribution of the alkoxide oxygen 2p orbitals to most other orbitals [96]. Consequently, their influence on the *syn/anti*-interconversion and reactivity of these complexes [97] was obvious. In contrast to the living polymerizations carried out with Mo-bis(hexafluoro-*t*-butoxide)-based initiators, which were found to yield all-*cis* polymers with only 75% tacticity [97], the living polymerizations that resulted from Mo-bis(*t*-butoxide)-derived initiators lead to the formation of all-*trans*, highly tactic polymers [98]. Tacticity of these polymers was suggested to be controlled by the chirality of the alkylidenes β -carbon (chain end control). Thus, among both rotamers of the Mo-initiator $\text{Mo}(\text{NAr})(\text{CHR})[\text{OCMe}(\text{CF}_3)_2]_2$, the *anti*-rotamer is the more reactive one in the reaction with bis(trifluoromethyl)norbornadiene (NBDF6), leading to a *syn*-first insertion product. The configuration of the double bond was determined as *trans* (*anti* \rightarrow *syn*, *trans*). In contrast, the *syn*-rotamer produces a *syn* first insertion product with a *cis*-configured double bond (*syn* \rightarrow *syn*, *cis*) (Scheme 5.9) [99].

Since little *anti*-form is present under equilibrium conditions (without irradiation) in $\text{Mo}(\text{NAr})(\text{CHR})(\text{OCMe}(\text{CF}_3)_2)_2$, and *syn*- into *anti*- conversion is slow (ca. 10^{-5} s^{-1}), *cis*-polymers are proposed to form from the *syn*-species of a catalyst via olefin attack on the CNO-face of the initiator [94]. In a *t*-butoxide system, where interconversion is relatively fast (ca. 1 s^{-1}), it was proposed that the *anti*-form was the only propagating alkylidene species. This proposal was further supported by studies carried out by Feast and co-workers [100]. Using sterically hindered and therefore unreactive monomers such as 1,7,7-trimethylnorbornene, only the reaction of the *anti*-rotamer at a very slow, monomer concentration-independent rate was observed. Additionally, the calculated rate constant was essentially identical with the one for *syn-anti*-conver-

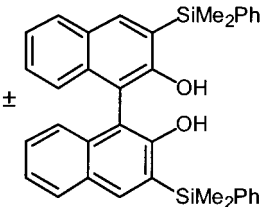
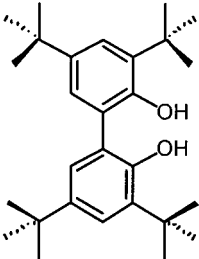
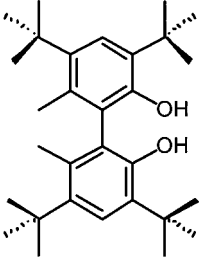
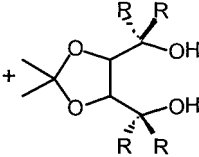


Scheme 5.9 Reaction of *syn*- and *anti*-rotamers in ROMP.
 Ar=2,6-*i*-Pr₂-C₆H₃, 2,6-Me₂-C₆H₃. R=*t*-Bu, CMe(CF₃)₂, etc.

sion. The high dependency of the *cis-trans* contents of a polymer on the temperature as found for the polymerization of NBDF6 or DCMNBD with Mo(N-2-*t*-Bu-C₆H₄)(CHCMe₂Ph){2,2'-[4,4',6,6'-*t*-Bu₄](C₆H₂)₂O₂} again underlined the importance of *syn-anti* conversion with respect to the time-scale of the polymerization [101]. Thus, the careful choice of an alkoxide in these systems offers an attractive access to polymers with either *cis*- or *trans*-configured double bonds as well as to highly tactic polymers [102]. While polymers prepared from Mo-based initiators containing non-fluorinated alkoxides such as *t*-butoxide are all-*trans* and highly tactic, polymers based on *cis*-vinylene units prepared from fluorinated analogues are usually only 70–75% tactic. In order to be capable of preparing polymers which are >99% *cis* and >99% tactic, the use of chiral alkoxide ligands was elaborated [103–105]. By this approach, polymerizations were forced to proceed exclusively via the *syn*-rotamer by an adjustment of the accessibility of the *trans*-rotamer. This was achieved by a subtle combination of the steric bulks of the phenoxide and arylimido ligands. Tab. 5.1 gives an overview over the corresponding chiral ligands, the investigated monomers and the polymer properties.

7-Oxanorbornene and 7-oxanorbornadiene-derivatives were found to form observable and even isolable molybdametallacycles. Thus, 7-oxa-2,3-(bistrifluoromethyl)norbornadiene reacts with Mo(N-2,6-*i*-Pr₂-C₆H₃)(CHCMe₃)(OCMe₃)₂ to form a remarkably stable metallacycle [106]. A similar tungstametallacycle was observed in the reaction of 2,3-bis(trifluoromethyl)norbornadiene with W(N-2,6-*i*-Pr₂-C₆H₃)(CHCMe₃)(OCMe₃)₂ [98].

Tab. 5.1 Representative examples of highly tactic polymers prepared from chiral alkoxides and phenoxides, initiators, and monomers.

Ligand (OR') ₂	Mo(NAr')(CHCMe ₂ R)(OR') ₂	Monomer	% cis/ % tacticity
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	NBDF6	>99/99
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	DMMNBE	>99/99
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph, THF-adduct	(2 <i>R</i> ,3 <i>R</i>)- BMCNBE	>99/93 <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph, THF-adduct	(5 <i>R</i> ,6 <i>R</i>)- BMMNBE	>99/91 <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph, THF-adduct	(5 <i>R</i> ,6 <i>R</i>)-DMNBE	95/95 <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	PLCONBDE	99/ <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	PLCONBDE	99/ <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph		
	Ar' = 2,6- <i>i</i> -Pr ₂ -C ₆ H ₃ , R = Me	MCNBD	99/96
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	MOCNBDE	99/ <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	MOCNBDE	99/ <i>iso</i>
	Ar' = 2,6-Me ₂ -C ₆ H ₃ , R = Ph	NBDF6	96/>99
 R = β-naphthyl	Ar' = 2,6- <i>i</i> -Pr ₂ -C ₆ H ₃ , R = Me	NBDF6	97/97

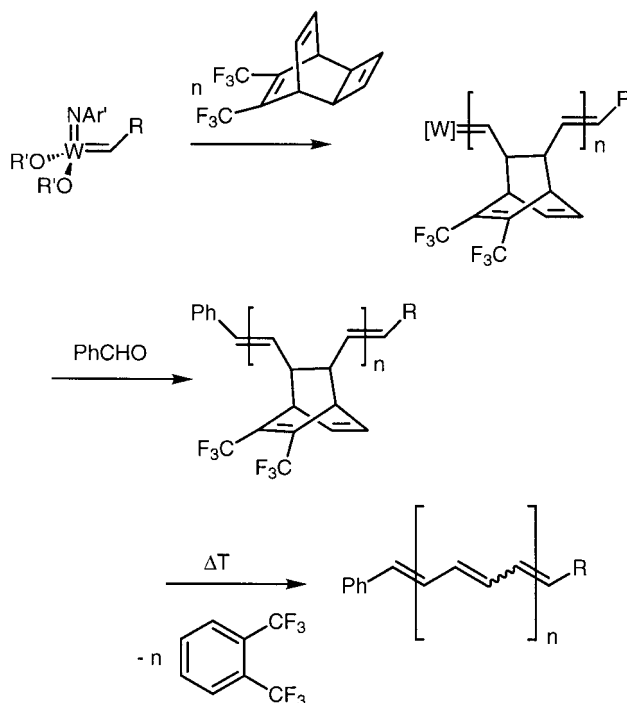
NBDF6 = 2,3-bis(trifluoromethyl)norbornadiene, DMMNBE = (+)-(2*S*,3*S*)-2,3-bis(dimethoxy-methyl)-norborn-5-ene, MOCNBDE = 2,3-bis((1*R*,2*S*,5*R*)-(-)-menthyloxycarbonyl)norbornadiene, PLCONBDE = 2,3-bis((-)-pantaloxyloxycarbonyl)norbornadiene, MCNBD = 2,3-bis(methoxycarbonyl)-norbornadiene, BMCNBE = 2,3-bis(methoxycarbonyl)norborn-5-ene, BMMNBE = 2,3-bis(methoxymethyl)norborn-5-ene, DMNBE = 2,3-dimethylnorborn-5-ene [102–104, 307].

Alkyne Polymerization by Molybdenum-imido-alkoxy-alkylidene Complexes

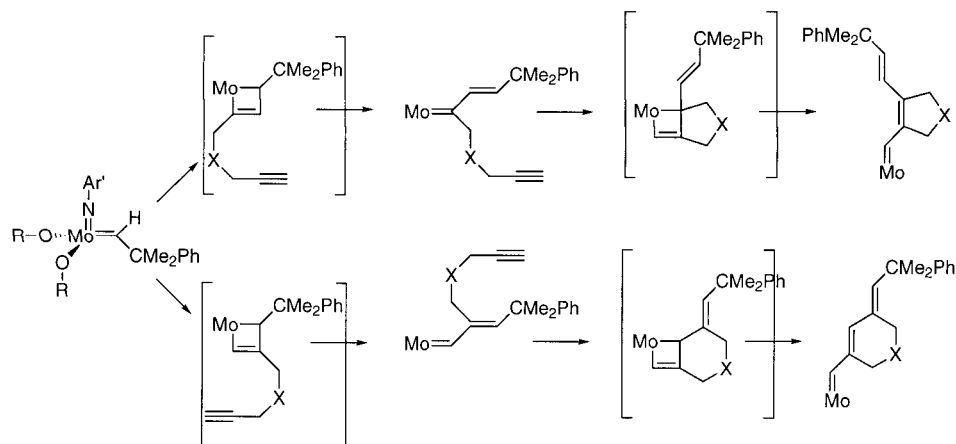
In principle, conjugated materials may either be directly synthesized via metathesis polymerization of acetylene or 1-alkynes, via ROMP of various cyclooctatetraenes (COTs) or via ROMP of polyene precursors as realized in the “Durham route” [107–111]. The first direct polymerization of acetylene to yield black untreatable unsubstituted polyacetylene was achieved with $W(N-2,6-i-Pr_2-C_6H_3)(CH-t-Bu)(OC-t-Bu)_2$ [112]. In order to obtain soluble polymers, polyenes were prepared via the ROMP of a polyene-precursor, 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDTF6), using initiators such as $W(N-2,6-i-Pr_2-C_6H_3)(CH-t-Bu)(OC-t-Bu)_2$ (Scheme 5.10) [113, 114].

The desired polyene was generated from the prepolymer by a thermally-induced retro-Diels-Alder reaction. The high degree of reaction control in this polymerization even allows the synthesis of oligomeric polyenes and their separation by RP-HPLC [108].

In contrast to unsubstituted acetylene, the polymerization of differently substituted 1-alkynes and di-1-alkynes may be carried out conveniently using Schrock-type catalysts. Dipropargylmalonate and derivatives thereof may be cyclopolymerized in a living manner using $Mo(N-2,6-i-Pr_2-C_6H_3)(CH-t-Bu)[OCMe(CF_3)_2]_2$. The



Scheme 5.10 Synthesis of conjugated polymers via the Durham route. $Ar' = 2,6-i-Pr_2-C_6H_3$, $R = t-Bu$.



Scheme 5.11 Cyclopolymerization of heptadienes. $X = C(COOEt)_2$, $C((1S, 2R, 5S)-(+)$ -menthyloxy-carbonyl), $C(COOEt)((1S, 2R, 5S)-(+)$ -menthyloxy-carbonyl).

resulting conjugated polymer contains both 5- and 6-membered rings, resulting from competitive α - and β -insertions (Scheme 5.11) [115, 116].

In accordance with the concept of “small” alkoxides elaborated for α -insertion [117, 118], a catalyst containing large carboxylate groups, $(Mo(N-2-t\text{-butylphenyl})(CH-t\text{-Bu})(O_2CCPh_3)_2)$, was found to produce a dipropargylmalonate-polymer which solely contained 6-membered rings [119]. Vice versa, catalytic systems that allow the synthesis of polymers consisting solely of 5-membered rings have been elaborated by our group [120]. Polyacetylenes with pendant metallocenyl side groups have been prepared by metathesis polymerization of the corresponding 1-alkynes [121–123]. Additionally, using 4-(ferrocenylethynyl)-4'-ethynyltolan [124, 125], the living character of an alkyne metathesis polymerization which proceeded via β -insertion was demonstrated for the first time [123]. In the case of linear n -alkyl-substituted alkynes the mode of insertion was reported to be governed solely by the electronic nature of the alkoxide. Thus, fluorinated alkoxides led to β -insertion, while the t -butoxide ligand favored α -insertion [126, 127].

Molybdenum and Tungsten Alkylidynes [128, 129]

The tungsten alkylidyne complex $(t\text{-BuO})_3W(C-t\text{-Bu})$ [130–132] is capable of catalyzing alkyne metathesis polymerization of cyclic alkynes. In addition, it can be used in acyclic diene metathesis (ADIMET) [133, 134]. The synthesis of the corresponding Mo-compound $Mo(CCH_2SiMe_3)(OAd)_3$ (Ad=adamantyl) has been reported by C.C. Cummins et al. [135]. Though the active species is not known yet, a mixture of $Mo(CO)_6$ and 4-chlorophenol is nowadays used for purposes of convenience [136].

5.2.3

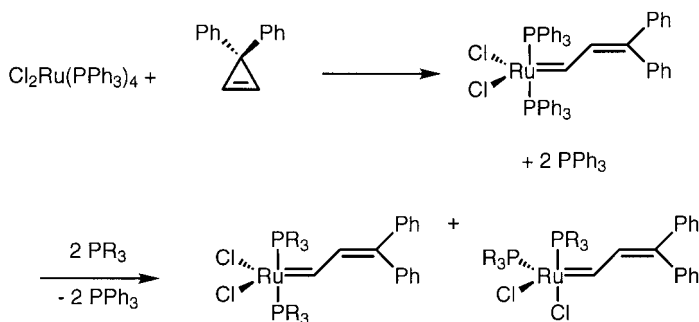
Group VIIA Transition Metal-Based Initiators**5.2.3.1 Rhenium-Based Initiators**

There exist various rhenium alkylidene and alkylidyne complexes such as $\text{Re}(\text{NAr}')_2(\text{CH}-t\text{-Bu})\text{Cl}$, $\text{Re}(\text{NAr}')_2(\text{CH}-t\text{-Bu})\text{OR}'$ ($\text{Ar}' = 2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3$, $\text{R}' = \text{OCMe}_3$, OCMe_2CF_3 , $\text{OCH}(\text{CF}_3)_3$, $2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3$) [137, 138], $\text{Re}(\text{NAr}')(\text{CH}-t\text{-Bu})(\text{OAr}')_3$ [139], $\text{Re}(\text{C}-t\text{-Bu})(\text{CHR}-t\text{-Bu})(\text{O}-t\text{-Bu})_2$ [140], $\text{Re}(\text{C}-t\text{-Bu})(\text{N}-2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3)[\text{OCMe}(\text{CF}_3)_2]_2$, $\text{Re}(\text{C}-t\text{-Bu})(\text{N}-2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3)(\text{OCMe}_3)_2$ [141–143], $\text{Re}(\text{C}-t\text{-Bu})(\text{CHR}-t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$ [144], $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_3\text{X}$ ($\text{X} = \text{OTf}$, C_6F_5 , BF_4) [145] and $\text{Re}(\text{C}-2,4,6\text{-Me}_3\text{-C}_6\text{H}_2)(\text{CO})_2(\text{O}_2\text{C}_2\text{Me}_4) \cdot \text{L}$ ($\text{L} = \text{PPh}_3$, pyridine) [146]. Unfortunately, none of them is active in ROMP or alkyne polymerization. Herrmann et al. introduced methyltrioxorhenium, CH_3ReO_3 , as a ROMP-active catalyst precursor [147]. Based on the results obtained by matrix photochemistry [148, 149], the polymerization-active species is believed to be the tautomeric form of CH_3ReO_3 , $\text{O}_2\text{Re}=\text{CH}_2(\text{OH})$.

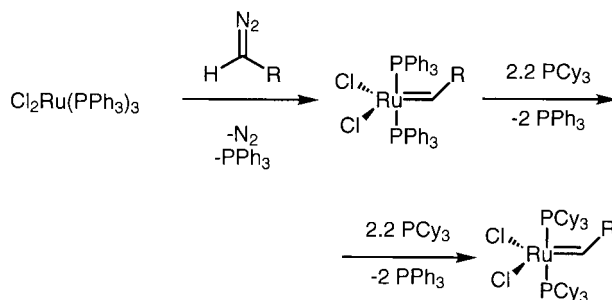
5.2.4

Group VIIIA Transition Metal-Based Initiators**5.2.4.1 Ruthenium-Based Initiators** [150]

Ruthenium salts such as $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ or ruthenium(II) tosylates have been known for long to effectively catalyze ROMP of several cycloalkenes. Despite the characterization of several olefin-ruthenium(II) complexes [151–154], the actual catalytic species in such systems is still ill-defined. Nevertheless, the fact that ruthenium-based systems did effectively catalyze the ROMP even in aqueous systems [155, 156] or in the presence of other protic functional groups (alcohols, carboxylic acids, etc.) [153, 154, 157–162] initiated an intense search for well-defined, functional group-tolerant ruthenium systems [163], mainly conducted by the group of R.H. Grubbs. In 1992, this group described the synthesis of the first well-defined ruthenium alkylidene (Scheme 5.12) [75].



Scheme 5.12 Preparation of the first well-defined ruthenium alkylidenes.



Scheme 5.13 Synthesis of first generation Grubbs-catalysts.

Thus, reaction of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ or $\text{Cl}_2\text{Ru}(\text{PPh}_3)_4$ with 2,2-diphenylcyclopropene in benzene or methylene chloride yields the desired ruthenium carbene complex in quantitative yield. Typical alkylidene resonances for H_a and C_a are observed at $\delta=17.94$ and 288.9 ppm (both in C_6D_6). Despite a ratio of $k_i/k_p < 1$, the compound was reported to be an efficient initiator for the polymerization of NBE. The rather low activity of the bis(triphenylphosphine) derivative for other cyclic olefins than NBE such as bicyclo[3.2.0]hept-6-ene or *trans*-cyclooctene was successfully enhanced by phosphine exchange with more basic analogues such as tricyclohexylphosphine and tri-*i*-propylphosphine (Scheme 5.12) [164].

It is worth mentioning that the resulting compounds of the general formula $\text{Cl}_2\text{Ru}(\text{CHCHCPh}_2)(\text{PR}_3)_2$ ($\text{R}=\text{cyclohexyl}$, *i*-propyl) exist in two isomeric forms as shown in Scheme 5.12. An alternative route to this initiator is the reaction of $(\text{PPh}_3)_3\text{RuHCl}$ with 3-chloro-3-methylbut-1-yne in $\text{CH}_2\text{Cl}_2\text{-AcCN}$. By this reaction, the acetonitrile-adduct of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_2(=\text{CH}=\text{CHCMe}_2)$ is obtained [165]. Finally, $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{P-}i\text{-Pr}_3)_2$ is accessible by a one-pot reaction of $\text{ClHRu}(\text{P-}i\text{-Pr}_3)_2$ with acetylene in $\text{HCl}/i\text{-propanol}$, followed by metathesis with styrene [166]. Among all these alternative routes, Schwab and Grubbs elaborated the probably most straightforward one that avoids the use of 2,2-diphenylcyclopropene [167, 168]. The synthetic protocol entails the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with a diazoalkane (Scheme 5.13).

The resulting compounds of the general formula $\text{Cl}_2\text{Ru}(\text{CHR})(\text{PR}_3)_2$ ($\text{R}=\text{Ph}$, CHCPh_2), nowadays well known as first generation Grubbs-catalysts, may be prepared in high yields. In analogy, a bimetallic species, $\text{Cl}_2\text{Ru}(\text{PPh}_3)_2\text{CH-}p\text{-C}_6\text{H}_4\text{-CHRu}(\text{PPh}_3)_2\text{Cl}_2$, may be prepared [169]. This initiator offers access to the formation of ABA *block*-copolymers.

5.2.4.2 Reactivity of Ruthenium-Based Initiators

Compared to molybdenum- or tungsten-based Schrock catalysts, the reactivity of ruthenium-based systems is different. While reactivity slightly increases in the order $\text{I} < \text{Br} < \text{Cl}$ [170] it may more efficiently be enhanced via the phosphines than by the nature of the alkylidene moiety [168] or by substitution of the chlorides by other, more electron-withdrawing, groups [171]. The thermodynamics and in par-

ticular the importance of σ -donation related with the exchange of phosphines, the influence of electronic as well as steric effects of this type of compounds have been studied in detail [172]. The stability as well as the reactivity order that may be deduced therefrom is $\text{PPh}_3 < \text{PBz}_3 < \text{PCyPh}_2 < \text{PCy}_2\text{Ph} < \text{P-}i\text{-Bu}_3 < \text{P-}i\text{-Pr}_3 < \text{PCy}_3$. The influence of different phosphines on the reactivity of ruthenium-based systems of the general formula $\text{Cl}_2\text{Ru}(\text{CHCHCPh})_2(\text{PR}_3)_2$ was additionally investigated in the ring-closing metathesis (RCM) of dipropargylmalonate [170]. These investigations again revealed increasing reactivity in the order $\text{I} < \text{Br} < \text{Cl}$ and $\text{PPh}_3 < \text{P-}i\text{-Pr}_2\text{Ph} < \text{PCy}_2\text{Ph} < \text{P-}i\text{-Pr}_3 < \text{PCy}_3$. In principle, two different mechanisms for the reaction of the initiator with an olefinic substrate were postulated on the basis of these experiments. These are an *associative*, with both phosphines on the metal center, and a *dissociative*, with only one phosphine attached to the ruthenium core. The finding that the addition of CuCl as a phosphine scavenger resulted in significantly elevated catalytic activities provided support for a dissociative mechanism. Investigations on the photoreactivity at $\lambda = 456 \text{ nm}$ of $\text{Ru}(\text{CHPh})\text{Cl}_2(\text{PCy}_3)_2$ revealed similar behavior, that is dissociation of one phosphine to form a trigonal bipyramidal structure [173]. Mechanistic studies by electrospray ionization (ESI) tandem-MS in the gas-phase support dissociation of one phosphine and suggested that the metallacyclobutane ring was a transition state rather than an intermediate [174]. Monophosphine adducts were also found to be the active species in ROMP carried out in the gas-phase [175]. Monophosphine or, generally speaking, mono-ligand adducts are unstable. Since such mono adducts are the actual catalytic species in metathesis-based reactions, the utility of any catalyst strongly depends on the ratio of the rate of catalysis to the rate of decomposition. Consequently, catalyst design has to focus on accelerating the catalytic process instead of accelerating both processes.

Interestingly, quantum molecular dynamics studies only suggested that both mono- and diphosphine adducts were stable enough to support both mechanisms [176]. Nevertheless, these calculations underlined the importance of the use of sterically crowded phosphines for the preparation of highly active ruthenium alkylidenes as they lead to longer and consequently less stable Ru-P bonds. The important effect of phosphine size and basicity on metathesis performance [170, 172] was further underlined by the finding that even small changes in the PCy_3 ligand allow the fine-tuning of this catalytic system. Thus, the use of the $\text{PCy}_2\text{CH}_2\text{SiMe}_3$ ligand allows the synthesis of the initiator $\text{Ru}(\text{CHPh})\text{Cl}_2(\text{PCy}_2\text{CH}_2\text{SiMe}_3)_2$ that turned out to be highly active in the polymerization of norbornene imides [177]. Quantitative measurements of the rate constants of phosphine dissociation and re-binding as well as on olefin insertion confirmed the dissociative mechanism. These studies further revealed that, in systems of the general formula $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PR}_3)_2$, phosphine exchange is much faster than the rate of reaction with olefin [178]. In addition, complexes with labile phosphines (PPh_3) exhibit the highest initiation rates [168] yet lowest polymerization activities. In order to be able to use the comparably reactive bis(tricyclohexyl) derivatives for ROMP in a way that quantitative initiation was achieved, a possibility to enhance initiation efficiency was greatly needed. The solution to this problem was found by addition

of additional free labile phosphine to $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$. This is made possible by the values of phosphine dissociation and the fact that initiation efficiencies governed by the ratio of the rate constants for initiation and propagation k_i/k_p can be tuned by addition of phosphine. This gives at least in principle access to living polymerization systems where molecular weights can be predetermined by the stoichiometry of the reactants [179].

Another important point that needs to be addressed in any catalytic system is its stability. Investigations carried out with a large variety of mono- and binuclear ruthenium alkylidenes revealed significant differences between the more stable alkylidenes and the rather unstable methylidenes [180]. In contrast to the corresponding unsubstituted molybdenum carbenes (Mo-methylidenes) [181] such as $\text{Mo}(=\text{CH}_2)(\text{NAr})(\text{OR})_2$, which are generally unstable, the analogous Ru-methylidenes ($\text{Cl}_2\text{Ru}(=\text{CH}_2)(\text{PR}_3)_2$) were reported stable in the solid state [168]. Such methylidenes are generally of significant importance in RCM as well as in ROMP in case chain-transfer agents (CTAs) are used. In $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PR}_3)_2$, alkylidene decomposition requires phosphine dissociation and is predominantly second order while methylidene decomposition in $\text{Cl}_2\text{Ru}(\text{CH}_2)(\text{PR}_3)_2$ turned out to follow primarily first order kinetics. Probably for steric reasons, no ethylene formation resulting from bimolecular decomposition is observed with methylidenes.

While the decomposition products of molybdenum-based initiators may conveniently be removed as molybdates after any metathesis reaction by addition of aqueous base, ruthenium tends to form RuO_2 , a black insoluble product. The removal of decomposed Ru-sites from any product is best performed by the use of a water-soluble phosphine such as tris(hydroxymethyl)phosphine [182]. Alternatively, addition of triphenylphosphinoxide or DMSO followed by filtration over silica was reported to be advantageous [183]. For purposes of completeness, the investigations of the actual catalytic cycle in the reaction of $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$ with cyclic olefins carried out with substituted cyclobutenes shall be mentioned [184].

Ruthenium-based Grubbs catalysts are highly efficient in the ROMP of various substituted cyclic olefins such as NBEs, bicyclo[3.2.0]heptene [185], 7-oxanorbornenes [186], in the presence of cationic surfactants [187] as well as for low-strain olefins such as cyclooctenes [188]. Interestingly, the polymerization of 7-*t*-butoxybicyclo[2.2.1]hepta-2,5-diene with $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$ does not lead to the desired polymer, but to cyclic products and regeneration of the initiator. So far, this exclusive cyclization has only been observed for this particular monomer [189]. Phosphine-exchange from the parent bis(triphenylphosphine) systems into the more reactive bis(tricyclohexylphosphines) may either be performed consecutively or *in situ*. In terms of stereoselectivity, polymers prepared from $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$ predominantly contain *trans*-vinylene units, usually in the range of 70–90% [190]. This percentage appears to be basically independent of temperature and solvent. Regioselectivity for unsymmetrically substituted NBEs such as *exo*-methylidene-NBE is generally low, only 7-substituted NBDEs are polymerized with *anti*-selectivity, that is with the substituent pointing away from the initiator. Usually, a strong isotactic bias is found for NBE-based monomers, NBDE-based analogues are usually less isotactic [190].

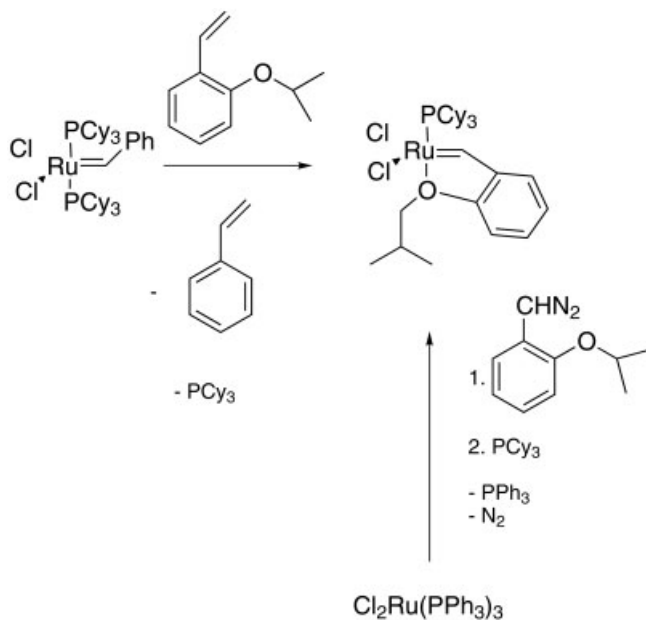
5.2.4.3 Ligand and Structural Variation in Ruthenium-Based Initiators

Variations in and Substitution of Phosphine-Ligands

The reaction of diazo-compounds with ruthenium arene complexes has been used for the *in situ* generation of ruthenium alkylidenes from $[\text{RuCl}_2(p\text{-cymene})]_2$, tricyclohexylphosphine and trimethylsilyldiazomethane [191]. The resulting initiators were again active in the polymerization of 2,3-difunctionalized NBDEs and their 7-oxa-analogues with high *trans*-stereoselectivity [192, 193]. Finally, following the diazo-approach, the synthesis of an internally oxygen-chelated ruthenium alkylidene has to be mentioned (Scheme 5.14).

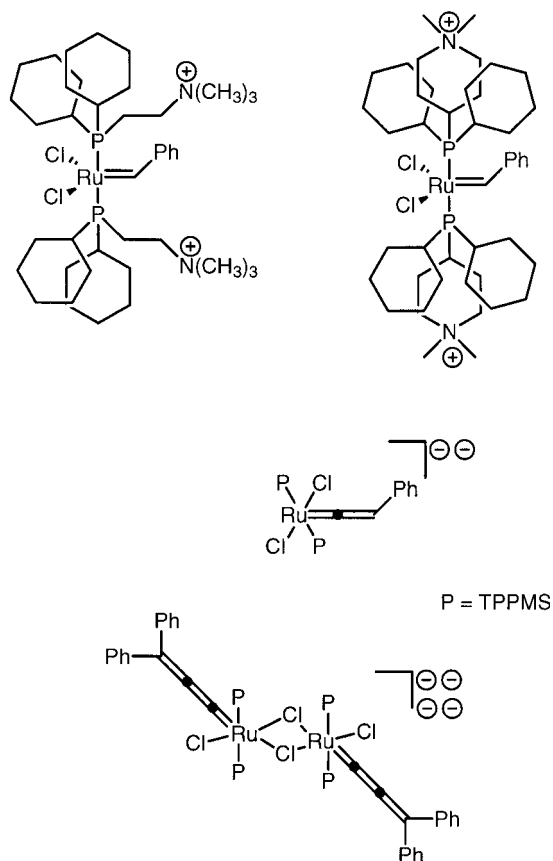
This compound, $\text{Cl}_2\text{Ru}(\text{CH-2-}i\text{-Pr-O-C}_6\text{H}_4)(\text{PCy}_3)$, is realized by reaction of $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ with 2-*i*-propoxyphenyldiazomethane/ PCy_3 . Alternatively, this complex, which turned out to be highly stable and even chromatographically recyclable, may be prepared by reaction of $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_3)_2$ with 2-*i*-propoxystyrene. So far, this compound, known as the “Hoveyda catalyst”, has only been used in RCM [194]. More recently, the synthesis of entirely water-soluble analogues has been reported (Fig. 5.5) [195–197].

With these systems, initiation of various substituted NBEs and 7-oxanorborn-5-enes occurs rapidly and quantitatively, yet polymerizations do not proceed in a living manner. In order to obtain truly living systems, investigations in terms of stability versus Brønsted acids such as DCl and bases were carried out [198]. Interestingly, and in contrast to the behavior of “classical” water-soluble systems such as



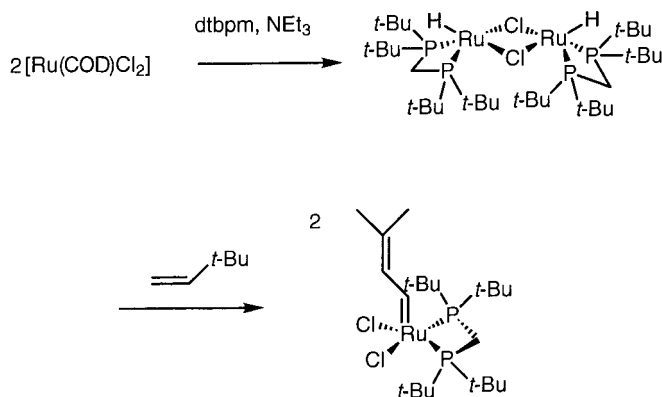
Scheme 5.14 Synthesis of an internally stabilized and chromatographically recoverable ruthenium alkylidene.

Fig. 5.5 Water-soluble Grubbs-type catalysts.



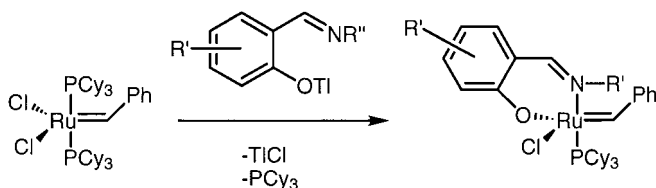
$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, addition of an acid does not interfere with the ruthenium alkylidene, but effectively protonates one phosphine group, thus generating a more active monophosphine complex. In *solution*, monophosphine adducts are stable under polymerization conditions and quantitatively initiate ROMP of cyclic olefins. Since first generation Grubbs type initiators including the water-soluble analogues are generally very sensitive versus $\text{pH} > 7$, polymerization in aqueous media can be carried out successfully in a truly living manner by adding small amounts of DCl (0.3–1 equiv. relative to the initiator). Polymers with PDIs (polydispersity indices) < 1.3 are obtained by this approach. Thus, by simply adding small amounts of DCl, the formation of hydroxide anions from the quaternary ammonium groups is successfully suppressed. In solvents with high dielectric constants, $\text{Cl}_2\text{Ru}(\text{CHPh})(\text{PCy}_2\text{R})_2$ ($\text{R} = \text{CH}_2\text{CH}_2\text{NMe}_3^+\text{Cl}^-$, $\text{N,N-Me}_2\text{-piperidin-4-yl}$) show non-destructive alkylidene proton exchange in D_2O or CD_3OD , presumably via dissociation of the halogen ligands [199].

Grubbs-type catalysts containing bridged diphosphino ligands were reported by several groups. Hoffmann and co-workers reported on the use of dtbpm (= di-*t*-butyldiphosphinomethane) based systems (Scheme 5.15) [200, 201].



Scheme 5.15 Synthesis of $[(\eta^2\text{-dtbpm})\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CMe}_2]$, dtbpm = di-*t*-butyldiphosphenomethane.

Though these systems were reported to be active in the metathesis polymerization of NBE, polymer yields were found to be comparably low (42%). Additionally M_w/M_n values of 2.75 suggested unfavorable ratios of k_i/k_p , resulting in a polymerization system where only a small part of the initiator initiates, while a major part remains inactive. In contrast to these *cis*-chelating systems, Fogg et al. reported on *trans*-bridged analogues based on diphosphines such as 1,4-bis(diphenylphosphino)butane (dppb), 1,4-bis(binaphthylphosphino)butane (binap), and 1,4-bis(dicyclohexylphosphino)butane (dcybp) [202, 203]. High activities and low polydispersities at least for NBE were reported. Interestingly, the polymerization mechanism was reported to be *associative* with both phosphines attached to the metal core. Other Ru-initiators containing chelating diphosphines such as 1,1'-diphosphenoferrrocene [204, 205] or xantphos [205] as well as dinuclear systems based on α,ω -bis(dicyclohexylphosphino)pentane and α,ω -bis(dicyclohexylphosphino)octane [205] have been reported, yet show comparatively low metathesis activity. The same is true for the Ru-ethylidene and vinylidene complexes $\text{Cl}_2\text{Ru}(\text{=CHCH}_3)(\text{PCoc}_3)_2$ and $[\text{RuHCl}(\text{=CCH}_2)(\text{PCoc}_3)_2]$ (Coc = cyclooctyl) described by Werner et al. [206]. Other structural variations in the synthesis of ruthenium carbenes including vinylidenes are obtained by the use of bidentate Schiff-base ligands (Scheme 5.16) [207],



Scheme 5.16 Synthesis of Schiff-base-ligated ruthenium carbenes.
 $\text{R}' = \text{H}$, 4- NO_2 , 6-Me-4- NO_3 , $\text{R}'' = 2,6\text{-i-Pr}_2\text{-C}_6\text{H}_3$, 2,6-Me₂-4-MeO-C₆H₃,
 2,6-Me₂-4-Br-C₆H₃, 2,6-Cl₂-4-CF₃-C₆H₃, 2,6-i-Pr₂-4- NO_2 -C₆H₃.

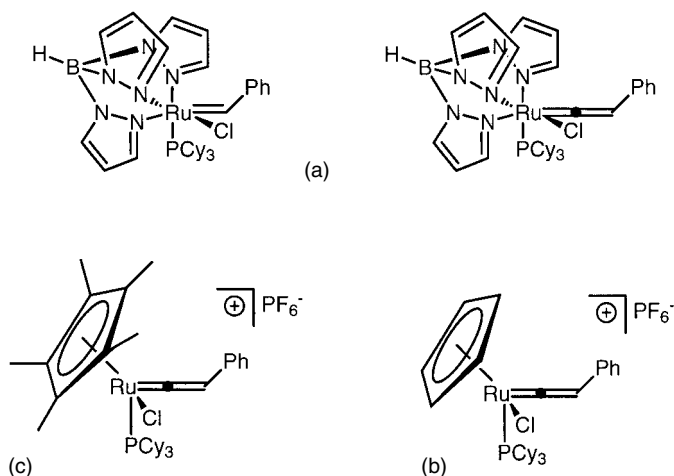


Fig. 5.6 Tris(pyrazolyl)borate- (a), cyclopentadienyl- (Cp-) (b), and pentamethyl-Cp- (c) based Grubbs-type catalysts.

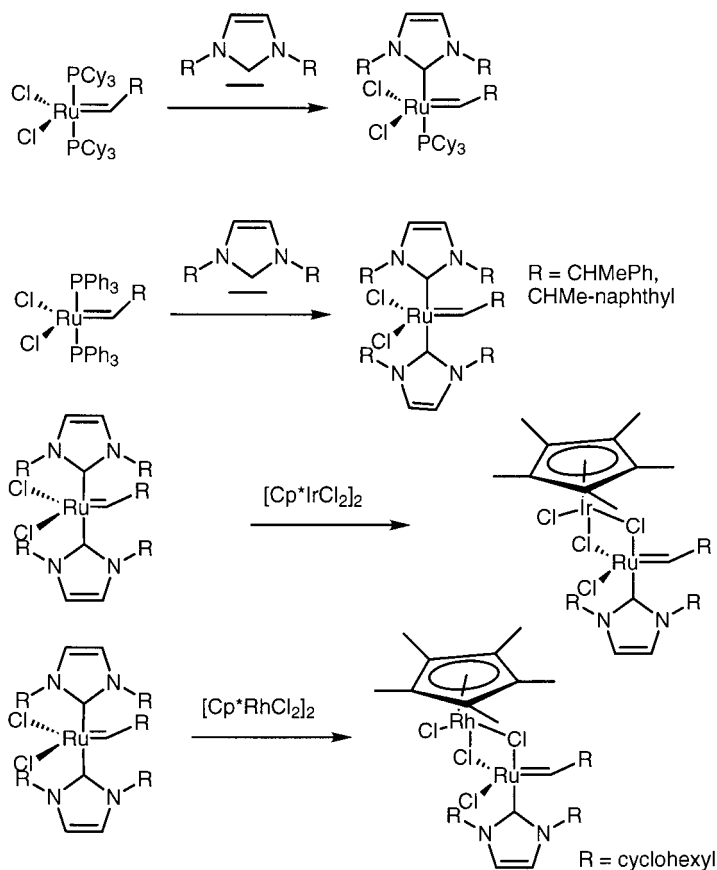
hydridotris(pyrazolyl)borate (Tp), cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (=pentamethyl-Cp) (Fig. 5.6) [208–212] and indenyl ligands [213].

In this context it is worth mentioning that $(\text{Tp}(\text{PPh}_3)(\eta^1\text{-O}_2\text{CCHPh}_2)\text{Ru}(\text{=CHPh}))$ is a (poor) catalyst for the ROMP of NBE without a co-catalyst, while molybdenum alkylidenes prepared from the Tp-ligand of the formula $\text{Mo}(\text{Tp})(\text{CHCMe}_2\text{Ph})(\text{N-2,6-i-Pr}_2\text{-C}_6\text{H}_3)(\text{OTf})$ require a co-catalyst (AlCl_3) in order to be ROMP active [214].

The most outstanding achievements in catalyst design have been accomplished by the use of N-heterocyclic carbenes (NHCs), a class of ligands developed by Wanzlick some 40 years ago [215]. Almost 20 years passed by from the synthesis of the first NHC-based-metal complexes [216, 217] to the isolation of the first stable, free NHC by Arduengo [218, 219]. Meanwhile their chemistry is well-understood [220–222], yet their enormous potential in catalysis has been recognized at a comparatively late stage [223–241]. NHCs are prepared either from glyoxal [242], by reduction of intermediary imidazole-2(3*H*)-thiones [243] or, in the case of the dihydro-analogues, from ethylenediamines and ethyl ortho-formate [244]. From the present point of view, the use of NHCs in ruthenium-based ROMP and RCM must be considered as a milestone in catalyst research [245].

Herrmann and co-workers first reported on the synthesis of mononuclear as well as binuclear NHC-based ruthenium alkylidenes [235] (Scheme 5.17).

An increased ROMP activity compared to mononuclear bis(phosphine)ruthenium alkylidenes [246] was found. A real breakthrough was the reaction of $\text{Cl}_2\text{Ru}(\text{CHR})(\text{PPh}_3)_2$ ($\text{R}=\text{Ph}, \text{CHCMe}_2$) with imidazoline-2-ylidenes [225, 227, 247] for the synthesis of ruthenium-based *mixed ligand* systems of the general formula $\text{Cl}_2\text{Ru}(\text{CHR})(\text{PR}_3)(\text{NHC})$ [231]. These imidazoline-2-ylidene-derived initiators turned out to possess dramatically elevated ROMP activities compared to the par-

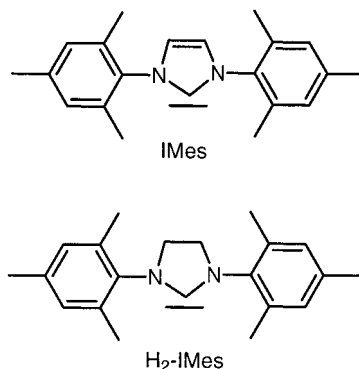


Scheme 5.17 Synthesis of chiral NHC-based mono- and binuclear ruthenium carbenes.

ent diphosphine and bis-NHC systems. This high activity is a direct result of the improved selectivity for binding π -acidic olefinic substrates in the presence of σ -donating free phosphine. The highest ROMP activities so far have been observed for the 1*H*-dihydroimidazol-2-ylidene derivatives (Fig. 5.7) [248]. The increased reactivity of these initiators is attributed to the lack of π -conjugation between the p_z orbitals of the double bond, the two N-atoms and the carbene present in the non-hydrogenated imidazol-2-ylidene ligand. This leads to an additional increase of electron density at the carbene.

Similar to the parent imidazol-2-ylidene compounds, the dihydro analogues are characterized by even lower initiation efficiencies, typically around 3–5% [248]. This is a consequence of the rather complex equilibria for phosphine dissociation, olefin coordination and insertion [177, 249]. Thus, substitution of one PCy_3 group in $\text{Cl}_2\text{Ru}(\text{CHR})(\text{PCy}_3)_2$ by the N,N' -dimesityl-1*H*-dihydroimidazoline-2-ylidene ligand decreases phosphine exchange by 2 orders of magnitude. Data on the ROMP activity of this class of compounds reveal the triphenylphosphine-containing systems as

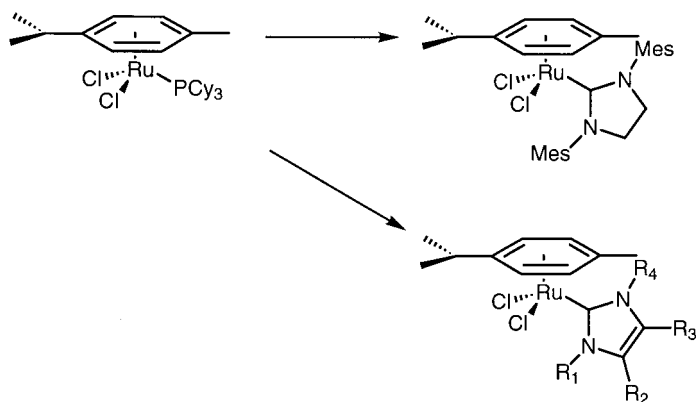
Fig. 5.7 Structures of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-2-ylidene (H₂-IMes).



the one with the highest ROMP and RCM activity. The rate constant for initiation was found to be completely independent of olefin concentration with a range of 0.172–1.02 mol olefin L⁻¹. This suggests that phosphine dissociation from these initiators is the rate-determining step for both ROMP and RCM. As a direct consequence, molecular weights cannot be controlled by stoichiometry of the reactants. Therefore, these systems, though highly active and functional tolerant, are rather used in RCM, cross-metathesis and ADMET than in ROMP. Reaction of Cl₂Ru(CHR)(PCy₃)(IMesH₂) with pyridine yields Cl₂Ru(CHR)(Py)₂(IMesH₂). This compound possesses labile halogens and, more importantly, labile pyridine groups that can easily be replaced by a variety of phosphines, thus offering an attractive synthetic route to new NHC-based initiators [250].

Other imidazole ligands, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol) and 1,3-bis(4-chlorophenyl)imidazol-2-ylidene (IpCl), were successfully used for the preparation of mixed-ligand ruthenium carbenes of the general formula Cl₂Ru(ChPh)(IMes)(L), L = PCy₃, PPh₃ [244, 251–253], and Cl₂Ru(CHCHCPh₂)(IMes)(PR₃), Cl₂Ru(ChPh)(ITol)(PR₃), Cl₂Ru(ChPh)(IpCl)(PR₃) [252].

Interestingly, NHC-based initiators can coexist with substituents at the 1 or 3 position of the NHC ligand that contain alkenes and C–H acidic sites [254]. The polymerization of 7-methylnorbornadiene and *exo*-7-methylnorborn-2-ene by a series of NHC-based initiators (Cl₂Ru(ChPh)(NHC)L, NHC = *N,N'*-dicyclohexylimidazolylidene, *N,N'*-bis((*R*)-naphthylethyl)imidazolylidene, *N,N'*-bis((*R*)-cyclohexylethyl)imidazolylidene, *N,N'*-bis((*R*)-phenylethyl)imidazolylidene, L = PCy₃, NHC, (*p*-cymene)RuCl- μ -Cl) revealed a comparatively high *cis*-content of the corresponding polymers (0.2 < σ_c < 0.70) [240]. All *cis*-units were found to be isotactic, while *trans* units are usually syndiotactic. Important in particular for reaction injection molding (RIM) is that NHC-containing catalyst precursors prepared from [RuCl₂(*p*-cymene)]₂ can serve as photoreactive systems that form the active species upon irradiation even at room temperature (Scheme 5.18) [255].



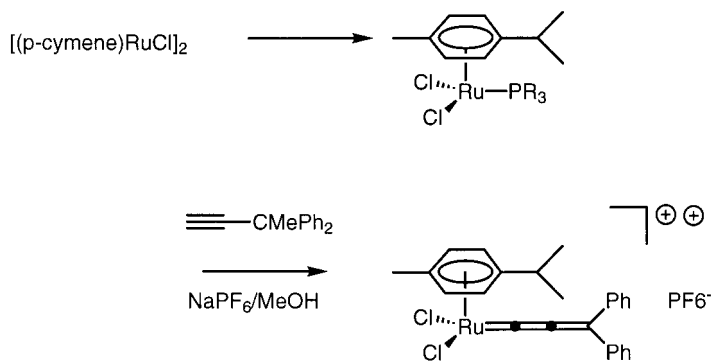
Scheme 5.18 Synthesis of photoreactive NHC-containing systems from $[\text{RuCl}_2(p\text{-cymene})]_2$.

Variation in the Alkylidene Moiety: Ru-Allenylidene, Vinylidene, Cumulenylidene, and Other Complexes

In principle, reactivity can be tuned by variations in the alkylidene moiety, too. Thus, different substituents and groups allow useful variations in k_i/k_p and give access to telechelic polymers. Rotational barriers have been calculated for vinylidene complexes of the general formula $\text{Cl}(\text{X})\text{Ru}(\text{=C=CHR})(\text{phosphine})_2$ by density functional theory calculations at the level of B3LYP [256]. Calculations suggest that the rotational barrier increases in the order $\text{X}=\pi\text{-acceptor} < \sigma\text{-donor} < \pi\text{-donor}$ ligand. Electron donating substituents at the vinylidene additionally increase the barrier of rotation. The IMes-derivative $\text{Cl}_2\text{Ru}(\text{C=CH-}t\text{-Bu})(\text{IMes})$ is best prepared from $\{[(p\text{-cymene})\text{RuCl}_2]_2\}$, $t\text{-Bu-acetylene}$ and the NHC and can be activated by a vinyl compound [257]. Ozawa and co-workers investigated the ROMP activity of a series of ruthenium vinylidene complexes [258]. NBE, 2,3-*endo,endo*-bis(methoxymethyl)NBE, 2,3-*endo,endo*-bis(methoxycarbonyl)NBE, 2,3-*exo,exo*-bis(methoxycarbonyl)-7-oxanorborn-5-ene, cyclooctene, as well as DCPD were successfully polymerized by $\text{Cl}_2\text{Ru}(\text{C=CH-}t\text{-Bu})(\text{L}_2)$ ($\text{L}=\text{P-}i\text{-Pr}_3$, PCy_3 , PPh_3). PDIs were in the range of 1.4–2.8, values for $M_n < 70\,000$.

A class of cationic ruthenium allenylidenes, recently reported by Fürstner and Dixneuf [259, 260], possesses similar high activity at least in RCM and presumably in ROMP. These cationic species are accessible by reaction of (*p*-cymene) $\text{RuCl}_2(\text{PR}_3)$ with a 1-prop-2-ynol, preferably with 1,1-diphenylprop-2-ynol (Scheme 5.19).

The efficiency (at least in RCM) of these 18 e^- allenylidene precatalysts depends on the nature of the counter anion. In particular the use of strongly electron-withdrawing substituents such as triflate improves their activity. It is worth mentioning that the catalytic activity of 16 e^- allenylidene complexes such as $[\text{Cl}_2\text{Ru}(\text{=C=C=CPh}_2)\text{L}^1\text{L}^2]$ ($\text{L}^1=\text{PCy}_3$, $\text{L}^2=\text{PCy}_3$, IMes) is much poorer (again at least in RCM) than that of the above-mentioned 18 e^- complexes [259]. Neutral di-

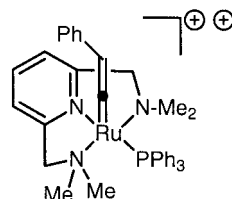


Scheme 5.19 Synthesis of RCM-active cationic ruthenium allenylidenes.
R=cyclohexyl, phenyl, i-propyl.

nuclear vinylidene complexes are accessible via reaction of $\text{Cl}_2\text{Ru}(\text{i-Pr}_2\text{CH}_2\text{CH}_2\text{OMe})_2$ with *m*-(HCC) $_2$ -C $_6$ H $_4$ [261]. A dicationic ruthenium vinylidene complex that was also reported to be active in the ROMP of NBE may be prepared from $[\text{RuCl}_2(\text{N},\text{N}',\text{N})(\text{PPh}_3)]$ and 2 equiv of AgBF_4 , (N,N',N)=2,6-bis[(dimethylamino)methyl]pyridine, (Fig. 5.8) [262].

Van der Schaaf and co-workers designed new heteroatom-containing Ru-carbenes, $\text{Cl}_2\text{Ru}(\text{CH-S-}p\text{-CH}_3\text{-C}_6\text{H}_4)(\text{P-i-Pr}_3)_2$, $\text{Cl}_2\text{Ru}(\text{CH-S-Ph})(\text{P-i-Pr}_3)_2$, $\text{Cl}_2\text{Ru}(\text{CH-CH}_2\text{CH}_2\text{-2-pyridyl})(\text{P-i-Pr}_3)_2$. These compounds were successfully used in the RCM of DCPD [263]. Variation in the gel time was accomplished by various methyl-substituents in the pyridyl ligand. Finally, complexes of the general formula $\text{Cl}_2\text{Ru}(\text{L})(=\text{CH-2-(i-Pr-OCO-)}\text{C}_6\text{H}_4)$, $\text{L}=\text{PCy}_3$, IMes were prepared for mechanistic studies [264].

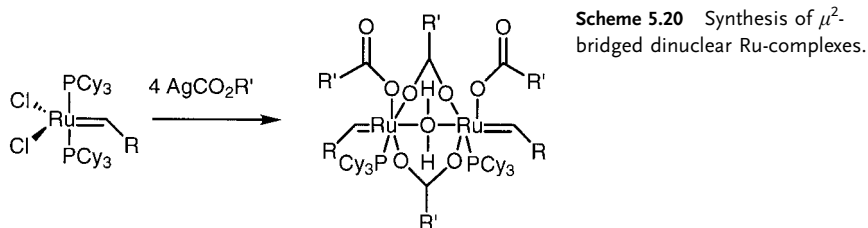
Fig. 5.8 Structure of 2,6-bis[(dimethylamino)methyl]pyridine- (= N,N',N-) based $\text{Ru}(\text{N},\text{N}',\text{N})(\text{CCHPh})$.



Variations by Substitution of the Halogen Ligands

$\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(=\text{CHR})$ ($\text{R}=\text{Ph}$, $\text{CH}=\text{CPh}_2$) reacts with silver salts of trifluoroacetic acid, pentafluoropropionic acid, pentafluorobenzoic acid and trichloroacetic acid to form binuclear μ^2 -carboxylato complexes (Scheme 5.20) [265].

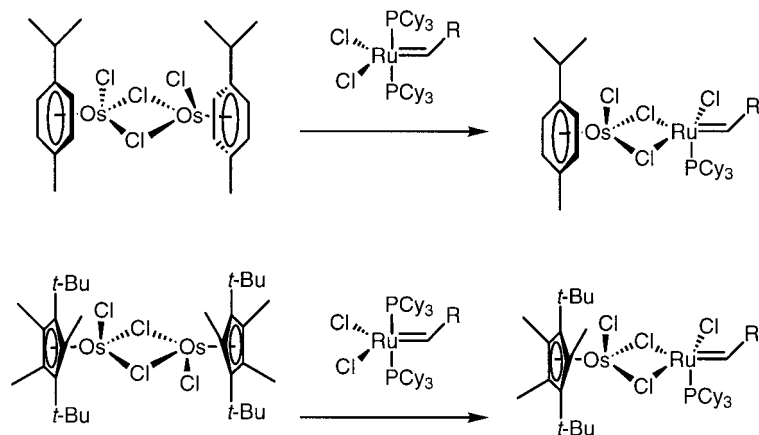
These complexes show metathesis activity, though detailed information of ROMP activity is not available. The same is true for $\text{ClRu}(\text{PCy}_3)_2(=\text{CH-2-Me-C}_6\text{H}_3\text{-6-O-})$, prepared from $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(=\text{CHPh})$ and 2,6-dimethylphenoxide [266]. A dicationic analogue of $\text{Cl}_2\text{Ru}(\text{PCy}_3)_2(=\text{CHCH}_3)$, $[\text{Ru}(\text{PCy}_3)_2(=\text{CHCH}_3)(\text{AcCN})]\text{X}_2$ ($\text{X}=\text{BF}_4$,



B(3,5-(CF₃)₂-C₆H₃)₄) was reported by Werner et al. [267]. Unfortunately, again no data on ROMP activity are available.

Heterobimetallic ruthenium alkylidenes, which may be prepared by reaction of Cl₂Ru(PCy₃)₂(CHR) with [Ru(*p*-cymene)Cl₂]₂, [Os(*p*-cymene)Cl₂]₂ and [Rh(*t*-butylcyclopentadienyl)Cl₂]₂ (Scheme 5.21), were reported to possess significantly elevated activities in the ROMP of 1,5-cyclooctadiene (COD) and 2,2-bis(trifluoromethyl)-norbornene [268]. Other ROMP-active initiators are the bimetallic complexes (*p*-cymene)RuCl(μ-Cl)₂RuCl(CHPh)(NHC) and (Cp*)RhCl(μ-Cl)₂RuCl(CHPh)(NHC) (NHC = N-heterocyclic carbene, Cp* = pentamethylcyclopentadienyl) [236, 237].

It is worth mentioning that the same compounds have been reported to be highly active in ring-closing metathesis (RCM) [238]. The reactivity of such systems increases in the order Ru < Os < Rh. Assuming that the coordination of the second metal center to the bridging chlorides directly influences their electron withdrawing capability, this finding is consistent with the observed order of activity I < Br < Cl in the mononuclear complexes [170].



Scheme 5.21 Synthesis of heterobimetallic ruthenium carbenes R = Ph.

5.2.5

Osmium-Based Initiators

Reaction of dineopentyl osmium dioxide with 2 equiv. of $\text{Ta}(\text{CHR})(\text{CH}_2\text{R})_3$ was reported to result in the formation of osmium dineopentylbisneopentylidene [269, 270]. Interconversion of the two isomeric forms (*syn-anti* and *anti-anti*) of this compound was postulated to proceed via an osmium tris(neopentyl)neopentylidene. So far, no reports on the ROMP activity of these complexes have been given. Similar to OsCl_3 [271] and $(p\text{-cymene})\text{OsCl}_2\text{P}(\text{c-H}_x)_3$ [272], $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ was reported to be active in the ROMP of NBE to yield all *cis*-poly-NBE [273].

5.3

Outlook

Future applications of both chiral molybdenum-based initiators currently investigated by Schrock and Hoveyda and NHC-based Ru-carbenes will clearly be situated in the area of organic synthesis [274–279]. This is particularly true for their heterogeneous analogues [193, 280–291]. From a realistic point of view, this polymerization technique will certainly not rival “traditional” polymerizations such as Ziegler-Natta- or metallocene-based chemistry. Nevertheless, ROMP, alkyne or ADMET polymerization certainly already hold their place in the synthesis of specialty polymers for both catalysis [291–293] and applications in materials [294] and life sciences [295–298], the more so as these techniques are additionally applicable to precipitation [299, 300], dispersion [301] and emulsion polymerization [302] as well as to polymerizations in supercritical CO_2 [303]. Tandem syntheses including consecutive ROMP [304], ADMET [305] or RCM [306] followed by catalytic hydrogenation by an *in situ* transformed Ru-catalyst additionally strengthen metathesis within the area of polymer synthesis. Once the problem of long-time stability of ROMP and ADMET polymers under ambient conditions is solved, a tremendous impact on polymer modification, in particular for polyolefins, can be expected.

5.4

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6

Catalysis in Acyclic Diene Metathesis (ADMET) Polymerization

STEPHEN E. LEHMAN Jr. and KENNETH B. WAGENER

6.1

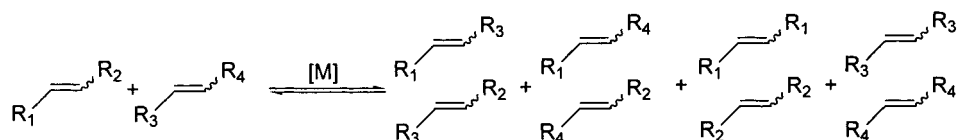
Introduction

Olefin metathesis (OM) has proven to be one of the most important advances in catalysis in recent years based on the application of this chemistry to the synthesis of polymers and biologically relevant molecules [1–10]. This unique transformation promotes chain and condensation polymerizations, namely ring opening metathesis polymerization and acyclic diene metathesis polymerization (ADMET). Applications of metathesis polymerization span many aspects of materials synthesis from cell-adhesion materials [11] to the synthesis of linear polyethylene with precisely spaced branches [12].

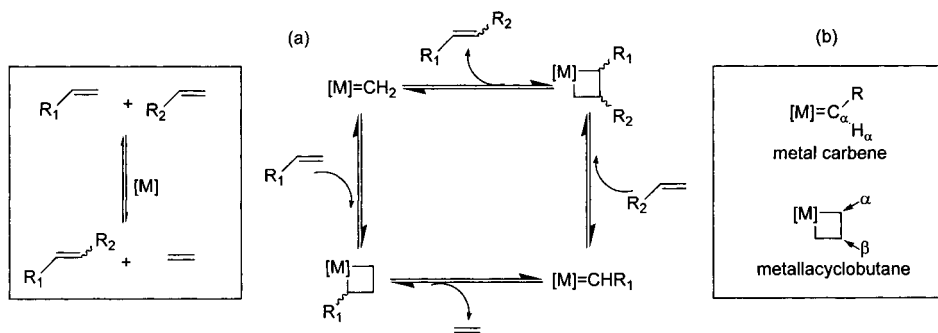
This chapter will present some of the history of ADMET and olefin metathesis in general, although the emphasis will be on the mechanism and kinetics of ADMET polymerization. The general mechanism for olefin metathesis will be presented before any of the specific catalyst structures are introduced or discussed in order to provide the reader with a firm basis upon which to compare the various popularly used catalysts for ADMET polymerization. In addition, procedural information will be given at the end of the chapter to give the reader an idea of what is specifically involved in a typical ADMET polymerization.

Olefin metathesis was first discovered during research stemming from Ziegler-Natta polymerization catalysis in the late 1950s [13–15]. The term olefin metathesis was not coined until 1967 [16]. Olefin metathesis is the apparent exchange of the carbons of olefins to produce new olefins. Empirically, this process can swap the substituents of olefins to give all possible products (Scheme 6.1).

This chemistry is always metal-catalyzed, and is presumed to proceed by a [2+2] cycloaddition of a metal carbene with an olefin to produce a metallacyclobu-



Scheme 6.1 The olefin metathesis transformation.



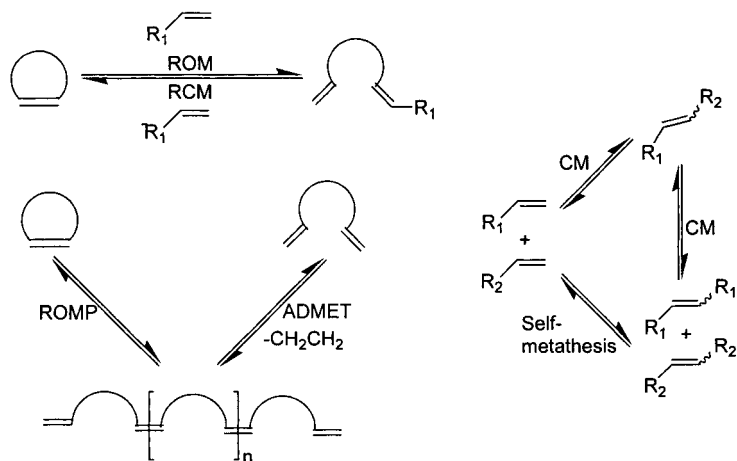
Scheme 6.2 (a) Chauvin mechanism of olefin metathesis for the coupling of two terminal olefins. (b) Nomenclature of positions for metallacyclobutanes and metal carbenes.

tane, followed by a [2+2] retro-cycloaddition to produce a new metal carbene and olefin (Scheme 6.2). All steps are reversible in principle.

For the early metathesis catalysts the active catalytic species are not spectroscopically identifiable, so speculation on the mechanism was the result of many careful experimental observations, particularly isotopic labeling studies [17]. Chauvin first proposed this mechanism in 1970 [18], and it was actively debated in the literature for some years after [19–22]. Substantial direct evidence, spectroscopic and otherwise, has been collected since that strongly supports the Chauvin mechanism. A major development in this field was made by the synthesis of highly metathesis-active well-defined early-transition metal carbene complexes by R. R. Schrock and others, since the active species for these systems are spectroscopically identifiable [23]. The mere fact that well-defined metal carbene complexes selectively promote olefin metathesis gave a great deal of credence to the Chauvin mechanism, and indeed this is the accepted mechanism for olefin metathesis today. Extension of this chemistry into the late-transition metals, particularly well-defined ruthenium complexes developed by R. H. Grubbs [24] and others, has augmented OM by adding the aspects of functional group tolerance and ease of handling.

Olefin metathesis is a versatile transformation, in that a number of distinct modes of reaction are possible (Scheme 6.3).

The generality and wide applicability of olefin metathesis is evident in that all of the possible modes of reaction have been used for various synthetic purposes. Ring-closing metathesis (RCM) is the intramolecular ring closing of a diene, and has found extensive employment in the construction of small, medium, and large rings for natural products syntheses [2, 3, 5–7, 25]. Ring-opening metathesis (ROM) is the reaction of a cycloolefin with another olefin to produce the ring-opened diene [26]. The chain polymerization of a cycloolefin to the corresponding acyclic polymer is termed ring-opening metathesis polymerization (ROMP). ROMP has been widely used to create polymers of all kinds [4]. Acyclic diene metathesis (ADMET) is the condensation polymerization of acyclic dienes, and has also been employed to create a variety of polymers, many of which cannot be pres-



Scheme 6.3 Some metathesis pathways.

ently synthesized by any other means. Cross metathesis (CM) is the metathesis of acyclic olefins to produce new acyclic olefins, and self metathesis is the reaction of two molecules of like olefin to give two new olefins. Cross metathesis has been used to rapidly construct synthetically useful functionalized olefins [27–30].

Olefin metathesis has been extensively written on in both books and journals [1–10]. This chapter will focus on ADMET. Of particular interest are the issues of catalysis, mainly functional group tolerance, kinetics, and mechanistic details. The development of late-transition metal catalysts has enormously expanded the scope of ADMET, so particular attention will be given to the well-defined ruthenium-based olefin metathesis catalysts. Pertinent information pertaining to catalysts of Group VI metals will also be provided. Important procedural aspects of ADMET will be presented in conclusion.

6.2

The ADMET Reaction

This section will cover the basic features of ADMET polymerization in order to provide a framework for consideration of the detailed aspects of the various metathesis catalysts to be considered in the next section.

6.2.1

ADMET: A Step-Growth Polycondensation

ADMET has been shown to be a step-growth polycondensation reaction [31]. The kinetics of step-growth polymerization and consequences thereof are completely different than those of chain polymerizations. Since ROMP and many other single-site transition metal-catalyzed polymerizations discussed in this book proceed

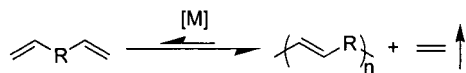
by a chain mechanism, it is relevant to cover the salient features of step-growth polymerizations as related to ADMET, although detailed discussions of step-growth polymerization are covered in a variety of excellent texts [32].

The kinetics of step-growth polymerizations demand that monomers of high purity be used in order to achieve high molecular weights [32]. The inclusion of even very small amounts of monofunctional impurities, monoolefins in the case of ADMET, has a detrimental effect on the polymerization as implied by manipulation (Eq. (1) below) of the Carothers equation, in which $\langle X_n \rangle$ is the number average degree of polymerization (DP), f_{imp} is the amount of monoolefin impurity as a fraction of the amount of diene monomer, and p is the extent of reaction as a fraction of unity. Assuming an extent of reaction of 0.99, the presence of 0.5% monoolefin impurity cuts $\langle X_n \rangle$ by 20%, from 100 to 80.2, and the presence of 1% impurity cuts $\langle X_n \rangle$ by 33% to 67. This equation also underlines the requirement of high extents of reaction. Assuming pure monomer ($f_{\text{imp}}=0$), slightly reducing p from 0.995 to 0.990 to 0.985 has the effect of reducing $\langle X_n \rangle$ from 200 to 100 to 67. This result underscores the necessity of removing the condensate molecule, ethylene in the case of ADMET.

$$\langle X_n \rangle = \frac{2 + f_{\text{imp}}}{2 + f_{\text{imp}} - 2p} \quad (1)$$

Given these rigorous demands for the success of a polycondensation reaction, there are several reasons why olefin metathesis is particularly well suited for polycondensation. The first is that although olefin impurities are detrimental to ADMET, other more common synthetic impurities are not, unless they react with the catalyst. Secondly, like most polycondensations, ADMET is a reversible process and removal of the condensate will shift the equilibrium towards higher molecular weight polymer. The condensate molecule for ADMET, ethylene, is a gas at room temperature and is thus readily removed from the reaction mixture to drive the reaction to high conversion (Scheme 6.4).

In the case of polyesterification, the condensate is water or an alcohol, which are somewhat more difficult substances to remove from the reaction. Removal of ethylene may be accomplished by applying vacuum to the reaction mixture or by passing an inert carrier gas over the reaction, although moderately high molecular weights can be achieved at room pressure without active removal of ethylene. For these reasons, high DP is attainable via ADMET, as demonstrated by a reported DP of almost 830 for the polymerization of 1,9-decadiene by a tungsten-based catalyst [31].



Scheme 6.4 Shifting ADMET equilibrium towards high molecular weight polymer by facile removal of ethylene.

6.2.2

Functional Group Tolerance

This treatment of polycondensation kinetics does not take into account the tolerance of the catalysts to impurities or to functional groups contained in the monomer. With many exceptions, metathesis catalysts are historically very sensitive to air, moisture, and some functional groups, although the advent of the late transition metal ruthenium-based catalysts has alleviated this problem to a great extent [1]. Nevertheless, several general features can be discussed. Firstly, all well-defined OM catalysts are sensitive to molecular oxygen to some extent. Secondly, separation of the double bond from both steric congestion and some functional groups is necessary. For example, many olefins with functionality directly bonded to the carbon-carbon double bond are not compatible with metathesis catalysts due to side reactions with the metal complexes [33]. Additionally, stable cyclic chelates of functionalized metal carbenes have been isolated [34], and thus separation of the olefin from coordinating functional groups in the monomer is generally desired to avoid the formation of stable five- and six-membered rings which may deactivate the catalyst or slow the rate of productive metathesis (Fig. 6.1).

This has been referred to as the “negative neighboring group effect” and has been proposed to be responsible for the slower kinetics of ADMET of ether dienes compared to hydrocarbon dienes [35]. Three carbons between the olefin and a carbon bearing coordinating functionality are usually sufficient to allow polymerization, although there are exceptions to this trend [33]. Intense catalyst development efforts are producing catalysts that are more and more tolerant to functionality closer to the olefin.

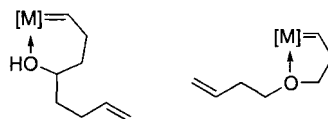


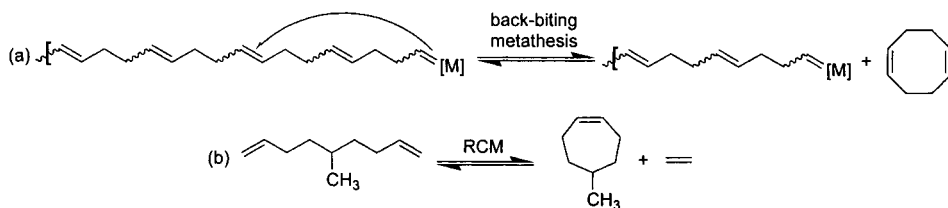
Fig. 6.1 Putative examples of metal-oxygen chelates.

6.2.3

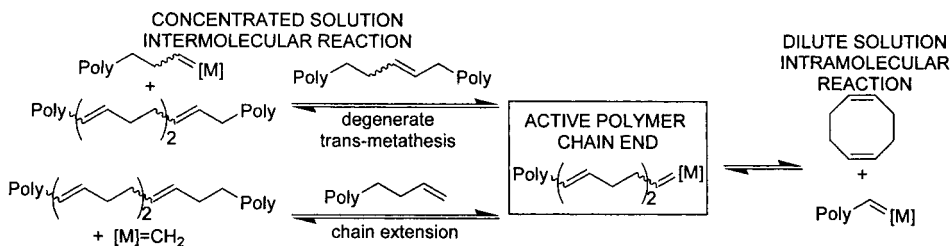
Formation of Cyclics

As with all polycondensation reactions, the formation of cyclic oligomers by ADMET is possible and has been demonstrated in a variety of cases [31–33]. This occurs by intramolecular back-biting metathesis of an active metal carbene with an internal olefin of the polymer (Scheme 6.5) to liberate cyclooctadiene, for example, from ADMET polybutadiene, although larger cyclics have also been observed. A related undesired cyclization is the intramolecular cyclization of the monomer by RCM.

Conducting ADMET in bulk monomer or in concentrated solution if the polymer or monomer is a solid minimizes both of these processes. Providing the



Scheme 6.5 (a) Back-biting metathesis of ADMET polybutadiene to produce cyclooctadiene (b) RCM of an ADMET monomer.



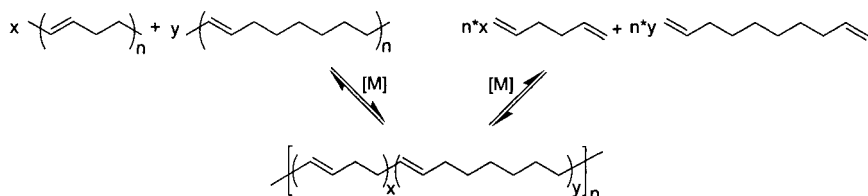
Scheme 6.6 Intermolecular processes occurring in concentrated solution and intramolecular process in dilute solution (Poly = polymer chain).

highest possible concentration of olefin chain ends promotes chain extension and degenerate intermolecular *trans*-metathesis, rather than intramolecular reactions (Scheme 6.6).

6.2.4

Trans-Metathesis

Degenerative *trans*-metathesis refers to reaction of an active chain end with an internal olefin of another polymer chain, and is also referred to as secondary metathesis. This process does not lead to increases in molecular weight or changes in the molecular weight distribution. Like other polycondensations, the molecular weight distribution of ADMET polymers should approach the most probable distribution (Flory distribution) and the polydispersity ($PDI = M_w/M_n$) should be approximately 2.0, both of which are observed experimentally [31–33]. Degenerative *trans*-metathesis was proven experimentally by combining independently prepared ADMET polybutadiene and ADMET polyoctenamer, and exposing the mixture to a metathesis catalyst. The resulting polymer is identical to the random copolymer produced by the ADMET of a mixture of 1,5-hexadiene and 1,9-decadiene (Scheme 6.7). This result can only be explained by metathesis with the internal double bonds of both polymers, which effectively randomizes the chemical structure to the observed copolymer [31].



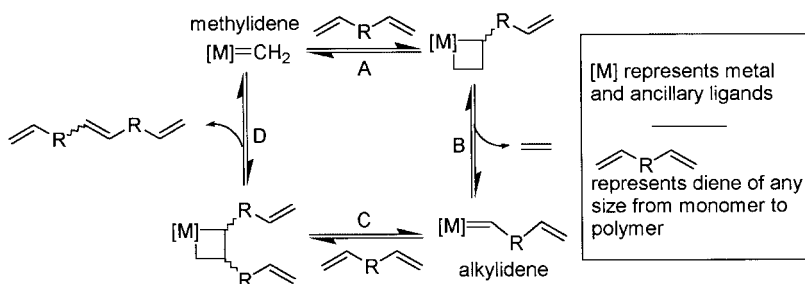
Scheme 6.7 Proof of the reversibility of ADMET and *trans*-metathesis.

6.2.5

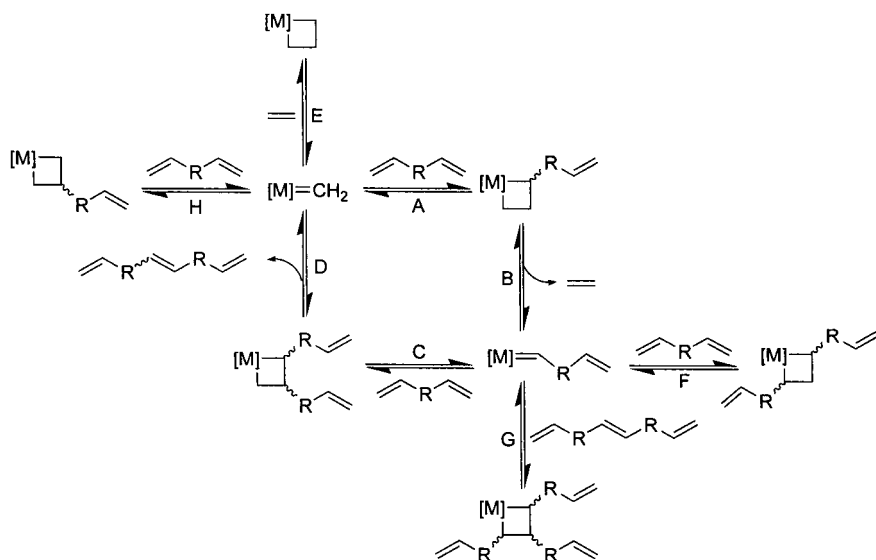
General ADMET Mechanism

Examining the mechanism of olefin metathesis uncovers a number of other issues associated with this catalysis (Scheme 6.8). The first point is that there are two distinctly different metal carbenes involved in the catalytic cycle; the metal methylidene and the metal alkylidene. The metal alkylidene is the metal carbene at the end of a polymer chain. Since the size of the polymer chain to which the metal is appended could affect reactivity, it could be stated that there are a great number of metal alkylidenes, corresponding to monomer, dimer, oligomers, and polymers of various lengths. It has been postulated that the size of the polymer chain affects the reactivity of the metal alkylidene to which it is attached due to increased steric shielding of the metal as the molecular weight increases, although this has not been proven experimentally in the context of ADMET [36].

Chain extension can only occur by the connection of two terminal olefins and is accompanied by the release of a molecule of ethylene, thus each chain extension event must start with the alkylidene and generate the methylidene (paths C and D in Scheme 6.8). Reaction of the methylidene with a terminal olefin regenerates the alkylidene and liberates the ethylene molecule (path A and B). Thus both the methylidene and the alkylidene are present in an ADMET reaction. The relative amounts of the methylidene and alkylidene in an ADMET reaction will depend on the rates of reaction of all steps in the cycle, principally the rates of reaction of the methylidene and alkylidene with a terminal olefin, and is thus a function of the particular catalyst used. Obviously the rates of both reactions should be as



Scheme 6.8 Generic catalytic cycle for productive ADMET.



Scheme 6.9 Mechanism of ADMET including non-productive pathways.

high as possible to favor the formation of high polymer. If either the methylidene or the alkylidene complex were inert towards metathesis with terminal olefins then the reaction would not proceed. The resting state of the catalyst in the cycle is also different for the various well-defined catalysts, but can be either the metal carbene or the metallacyclobutane [37].

The mechanism depicted in Scheme 6.8 only considers the productive metathesis mechanism. Four other pathways must be considered (Scheme 6.9).

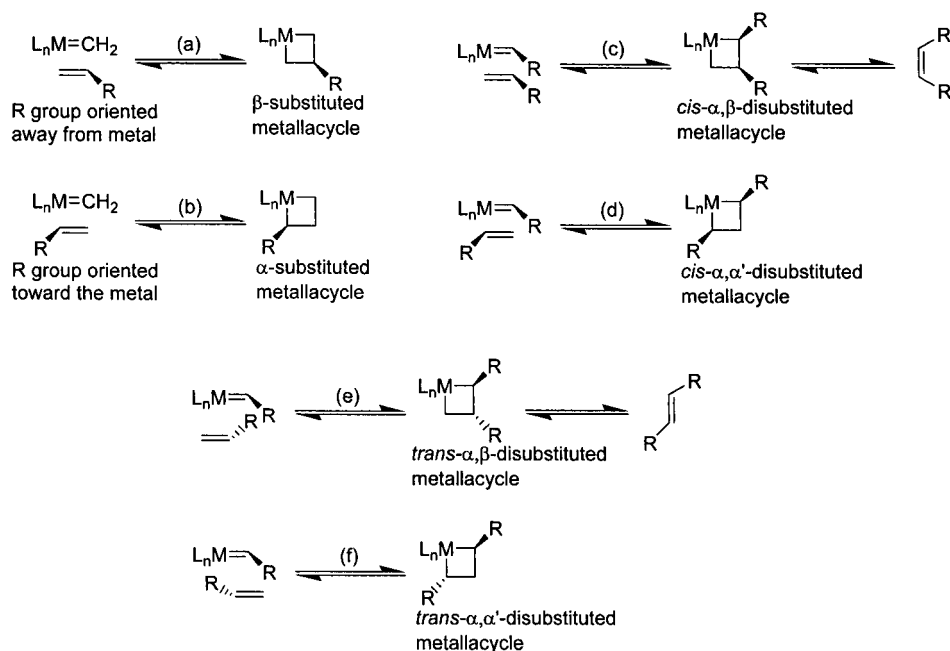
Two of these are the cycloaddition of the methylidene with ethylene (path E, non-productive), reaction of the methylidene with an internal olefin such that the alkyl substituent on the metallacyclobutane is in the β -position (path H, non-productive). The other two pathways are the cycloaddition of the alkylidene with an internal olefin to give the trisubstituted metallacyclobutane (path G, *trans*-metathesis, non-productive) and the reaction of the alkylidene with a terminal olefin to give the α,α' -disubstituted metallacyclobutane (path F), which can be looked at as a chain transfer-type event, albeit not in the sense of a chain polymerization. In this case, the alkylidene is shifted from the end of one chain to the end of another chain. So, assuming that all pathways have somewhat similar rates, the elimination of ethylene will drive the reaction to high polymer. In the case of ADMET, these additional mechanistic pathways do not prevent the polymerization reaction, since these additional pathways are either degenerate or represent processes that do not affect the overall molecular weight distribution of the polymer.

6.2.6

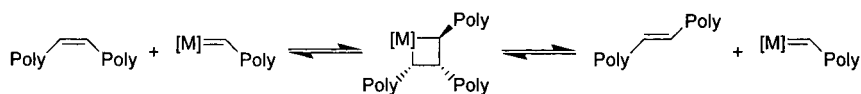
Regiochemical and Stereochemical Considerations

Paths F and H in Scheme 6.9 are based on different regiochemical orientations of the cycloaddition reactions. The olefin and the carbene must be oriented cofacially prior to the cycloaddition to form the metallacyclobutane ring, so the different stereochemical pathways possible can be modeled (Scheme 6.10).

The preferences of the various pathways are dependent on the catalyst used, specifically the electronic and steric factors involved. The electronic contribution is based on the preference of the metallacycle to have the electron-donating alkyl groups at either the α or the β carbon of the metallacycle [23]. The steric factors involved in the approach of the olefin to the metal carbene also determine the regiochemistry of the metallacyclobutane formed. These factors include both steric repulsion of the olefin and carbene substituents from each other and from the ancillary ligands of the metal complex. Paths (b), (c), and (e) in Scheme 6.10 are important to productive ADMET. The relative rates of pathways (c) and (e) will determine the kinetic amount of *cis* and *trans* double bonds in the polymer chain. However, in some cases a more thermodynamic ratio of *cis* to *trans* olefin isomers is attained after long reaction times, presumably by a *trans*-metathesis olefin equilibration mechanism [31] (Scheme 6.11).



Scheme 6.10 Some stereochemical pathways of metathesis.



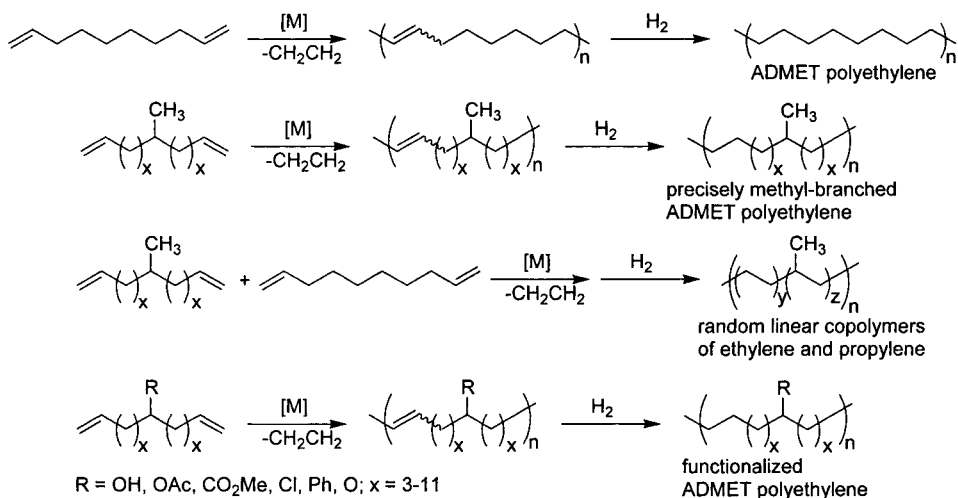
Scheme 6.11 Olefin equilibration via *trans*-metathesis.

6.2.7

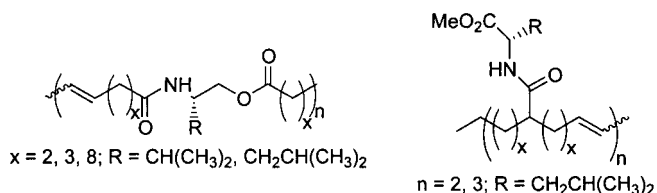
Applications of ADMET

ADMET has found a variety of applications, mostly based on the synthesis of novel linear polymers. Generally speaking, ADMET is particularly useful for synthesizing linear polymers with functionality or structure separated by a length of methylene units and a carbon-carbon double bond [38–43], although conjugated [44, 45] and other polymeric structures [46] have also been synthesized via ADMET. Comprehensive reviews exist in the literature [47, 48], so only a few examples of these polymers will be given here. Saturated polymers resulting from hydrogenation of the carbon-carbon double bonds of ADMET polymers are desirable materials, and a very useful sequential one-pot homogeneous ADMET heterogeneous hydrogenation technique exists to perform this reduction [49].

Recently, much attention has been devoted to modeling polyolefins and copolymers of ethylene and polar monomers. For example, polymers with regularly spaced methyl groups on a polyethylene backbone have been synthesized and display very interesting and surprising thermal properties and microstructure [12]. This represents a rational synthesis of branched polyethylene that cannot be achieved by any other means at this time (Scheme 6.12).



Scheme 6.12 Synthesis of ADMET polyethylene and ethylene-propylene copolymers.



Scheme 6.13 Synthesis of amino acid containing ADMET polymers.

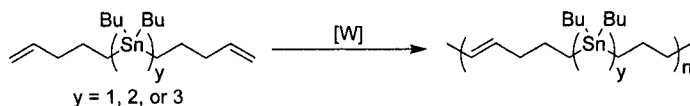
These materials can be considered linear copolymers of ethylene and propylene or precisely methyl-branched polyethylene. In addition, copolymerizations of the methyl-containing monomers with 1,9-decadiene yield polymers with lower propylene content [50]. These materials are of great interest to the polyolefin community, especially in the physical understanding of the effects of branching on physical properties. Polyethylenes with a variety of main chain functionality have also been synthesized and analyzed [51–54].

Another area of active research is the synthesis of main-chain and side-chain amino acid-containing polymers for various biological applications. These chiral polymers are novel structures and represent the fusion of polyolefins and peptides [55, 56] (Scheme 6.13).

6.3

Classical Metathesis Catalysts

Several early attempts at ADMET polymerization were made with “classical” olefin metathesis catalysts [57–59]. The first successful attempt was the ADMET polymerizations of 1,9-decadiene and 1,5-hexadiene with the $\text{WCl}_6/\text{EtAlCl}_2$ catalyst mixture [60]. As mentioned in the introduction, the active catalytic entities in these reactions are ill-defined and not spectroscopically identifiable. Ethylene was trapped from the reaction mixture and identified. In addition to the expected ADMET polymers, intractable materials were observed, which were presumed to be the result of vinyl polymerization of the diene to produce crosslinked polymer. Addition to double bonds is a common side reaction promoted by classical olefin metathesis catalysts. Indeed, reaction of styrene with this catalyst mixture and even with WCl_6 alone led to polystyrene. Years later, “classical” catalysts were revisited in the context of producing tin-containing ADMET polymers with tungsten phenoxide catalysts [61]. Alkyl tin reagents have long been known to act as co-catalysts in classical metathesis catalyst mixtures, and in this case the tin-containing monomer acted as monomer and co-catalyst [62]. Monomers with less than three methylene spacers between the olefin and tin atoms did not polymerize (Scheme 6.14).



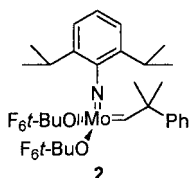
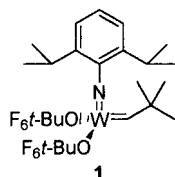
Scheme 6.14 Polymerization of organostannanes with classical metathesis catalysts.

6.4

Well-Defined Tungsten and Molybdenum Catalysts

The applicability of ADMET was greatly expanded by the development of well-defined catalysts by R. R. Schrock and co-workers. These catalysts promote metathesis without added Lewis acid co-catalysts, and thus eliminate the vinyl addition chemistry that was observed for the $\text{WCl}_6/\text{EtAlCl}_2$ catalyst. Complexes **1** [23, 63] and **2** [64, 65] have been used extensively for ADMET polymerizations. These complexes are pseudotetragonal and the carbene fragment tends to point towards the imido ligand (*syn*-rotamer), although the opposite rotamer (*anti*-rotamer) is also observed.

This general type of metal carbenes is termed “Schrock carbenes”. These carbenes differ from Fischer carbene complexes (those with α -hetero-substituents) in a number of ways. Schrock carbenes are viewed as X_2 ligands with +2 charge, whereas Fischer carbenes are considered neutral L ligands. Fischer carbenes are electrophilic at the α -carbon and Schrock carbenes are nucleophilic. Thus complexes **1** and **2** are formally W(VI) and Mo(VI) complexes [66].



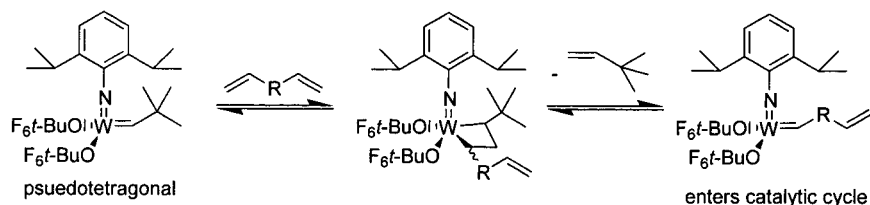
There are a number of differences between the tungsten and molybdenum complexes. The main generality drawn from the data is that the tungsten complexes promote olefin metathesis quite a bit faster than the molybdenum complexes, but the tungsten complexes are less tolerant of functionality. The tungstacyclobutane is more stable than the molybdacyclobutane. Several tungstacyclobutanes have

been isolated and unambiguously characterized. Both complexes are catalytically sensitive to air and moisture.

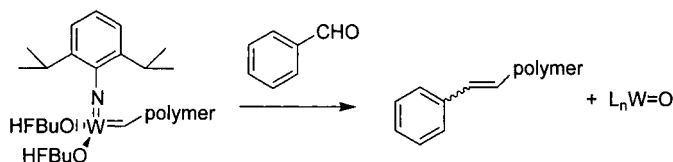
The alkoxide ligands play a critical role in the metathesis activity of these complexes. As a general rule, the metathesis of strained cyclic olefins (ROMP) is a much more facile process than the metathesis of acyclic olefins (ADMET). Thus, most metathesis catalysts will catalyze ROMP while only a fraction of these will catalyze ADMET. In these complexes, altering the alkoxide ligands controls the metathesis activity. The general trend is that the more electron-withdrawing (within limits) the alkoxide ligand is, the higher the metathesis activity of the complex. The reaction of the metal carbene on an olefin is best described as an electrophilic attack, and thus a more electron-poor metal center will favor the electrophilic attack. Control of reactivity of these complexes is perhaps best shown by the fact that the bis-*t*-butoxide analog of complex 2 catalyzes living ROMP (controlled MW, low PDI), while complex 2 itself catalyzes ROMP in a much less controlled manner (high MW, broad MW distribution). The metathesis activity of the bis-*t*-butoxide analog is lower than that of 2, such that initiation (first turnover) of the catalyst occurs faster or at approximately the same rate as propagation. For complex 2 itself, propagation is faster than initiation, leading to a less controlled polymerization [67]. In the case of acyclic olefins, the bis-*t*-butoxide analogs of 1 and 2 are unreactive, whereas complexes 1 and 2 do catalyze the metathesis of acyclic olefins, including ADMET.

The tungsten complex 1 was used to synthesize a variety of ADMET polymers including silicon and ether-containing materials [31, 33]. The double bonds of the resultant polymers are predominantly of the *trans* configuration (75–95%, typically over 90%) [31]. The initial alkylidene is lost in the first turnover of the reaction to afford the alkylidene complex that enters the catalytic cycle (Scheme 6.15).

Tungsten carbenes of this type will react with a variety of functional groups to destroy the metathesis activity of the complex. Most notably, these carbene complexes will react with aldehydes, ketones, and even esters in a Wittig fashion to give the tungsten-oxo complex and olefin [23]. This aspect of these complexes has been exploited as an easy way to define the end groups of ROMP polymers. For example, addition of benzaldehyde to a growing ROMP polymer yields a polymer with a well-defined, observable phenyl end group [67] (Scheme 6.16). This end-capping procedure can also be used for ADMET, although typically the reaction mixture is simply exposed to air to oxidize the remaining alkylidene.



Scheme 6.15 Loss of original carbene (neopentylidene) during first catalyst turnover.



Scheme 6.16 Use of benzaldehyde as polymer end-capping reagent.

The molybdenum catalyst **2** has been used extensively for ADMET polymerization. This complex is easier to handle than the tungsten analog and is more tolerant of functionality. This complex has allowed the synthesis of polymers containing esters, carbonates, ethers, sulfides, aromatic amines, boronates, dichlorosilanes, siloxanes, acetals, and conjugated carbon-carbon double bonds [38–45]. Aldehydes, ketones, and protic functionality are not tolerated. The molybdenum alkylidene will react with aldehydes and ketones, but not esters, in a Wittig fashion [64].

Both of these complexes can be used in ADMET polymerizations at temperatures up to approximately 55 °C, although decomposition certainly occurs over the time scale of a typical ADMET polymerization (days). A structure-reactivity study was performed on complexes **1** and **2** that revealed a number of features of these complexes [68]. Notably, **2** will polymerize dienes containing a terminal and a 1,1-disubstituted olefin, but never produces a tetrasubstituted olefin. One of the substituents of the 1,1-disubstituted olefin must be a methyl group. In contrast, complex **1** will not react with a 1,1-disubstituted olefin. The tungsten complex is more reactive towards internal olefins than external olefins [23, 63] indicating that secondary metathesis, or *trans*-metathesis, probably dominates the catalytic turnovers in ADMET with complex **1**.

The high *trans* content witnessed in ADMET polymers produced by these catalysts can be explained by the preference of the all-pseudoequatorial configuration in the metallacyclobutane intermediates, which is suggested by NMR and X-ray data [23] (Fig. 6.2). The all-equatorial conformation of the metallacyclobutane leads to the production of *trans* olefins.

Complex **2** is still regarded as the best catalyst for the polymerization of hydrocarbon ADMET monomers and monomers containing other tolerated functional groups, if the monomers can be rendered rigorously dry and oxygen-free. The ac-

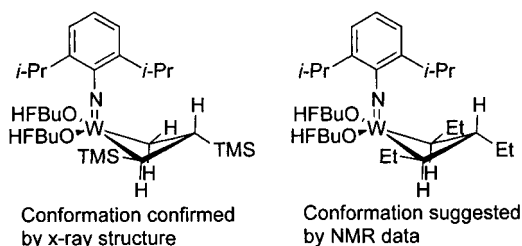


Fig. 6.2 Structures showing preference of all-equatorial tungstacyclobutanes.

tivity of these complexes in ADMET has yet to be surpassed by late-transition metal complexes, although new catalysts are promising.

6.5

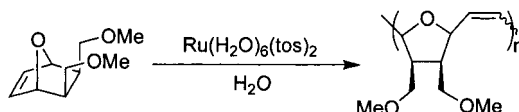
Well-Defined Ruthenium Catalysts

The drive to move further to the right in the periodic table is to develop functional group-tolerant catalysts that are less sensitive to air and moisture than complexes of high oxidation state early-transition metals. The Group VI metals of complexes **1** and **2** are in the highest oxidation state and, correspondingly, are highly oxophilic, which leads to protic and coordinating functional group intolerance and sensitivity to air and moisture. As a general rule, organometallic complexes of late transition metals are more stable to air, moisture, and functional groups than the early metals in high oxidation states [66]. Schrock and co-workers prepared some well-defined Re(VII) complexes that catalyze metathesis, but the metal is still in the highest oxidation state, d^0 electron configuration and is thus somewhat oxophilic [69]. The beginning of the development of well-defined late-transition metal OM catalysts came with studies on ROMP catalyzed by ill-defined ruthenium catalysts by Grubbs and co-workers, and led to the development of well-defined ruthenium carbene complexes capable of catalyzing olefin metathesis.

6.5.1

Early Observations: Ill-Defined Ruthenium-Based Catalysts

There were several reports of ROMP with Group VIII metals between 1965 and 1982 [70–73]. These studies were reinitiated in the late eighties by the Grubbs group with the report that 7-oxanorbornene derivatives underwent ROMP promoted by RuCl_3 , $\text{Ru}(\text{COD})\text{Cl}_3$, and OsCl_3 in benzene solution [74]. Polymerizations using these catalysts required a long initiation period, ranging from hours to days, before the monomer was rapidly consumed. It was then discovered that the presence of water decreases the initiation time for these complexes and thus acts as co-catalyst. Upon polymerization in water as solvent, initiation periods were reduced to 30 min and MW of polymers increased up to four-fold compared to the polymerization in organic solvents. The aqueous media used for these polymerizations was recyclable for up to 14 batch polymerizations and the initiation period steadily *decreased* to a lower limit of 10 s upon recycling. The Ru(II) complex $\text{Ru}(\text{H}_2\text{O})_6(\text{tos})_2$ ($\text{tos} = p\text{-toluenesulfonate}$) was found to be more active than Ru(III) or Ru(IV) precursors [75] (Scheme 6.17). This complex also catalyzes the isomerization of olefins, another typical side reaction of classical metathesis catalysts, by an allylic mechanism demonstrated by isotopic labeling experiments [76]. The activity of these complexes are limited to the ROMP of strained cyclic olefins, and thus they do not promote ADMET.



Scheme 6.17 ROMP of 7-oxanorbornene derivative in water.

6.5.2

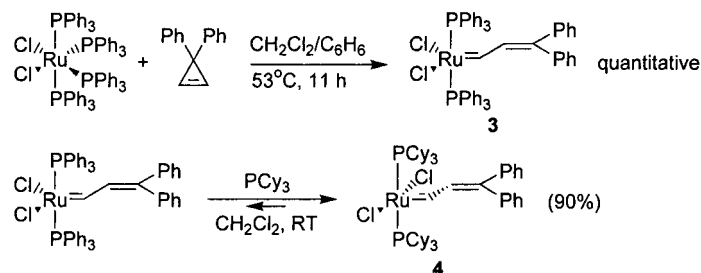
First-Generation Grubbs Catalysts: $\text{RuCl}_2(\text{PR}_3)_2\text{CHR}_1$

6.5.2.1 Synthesis and Activity

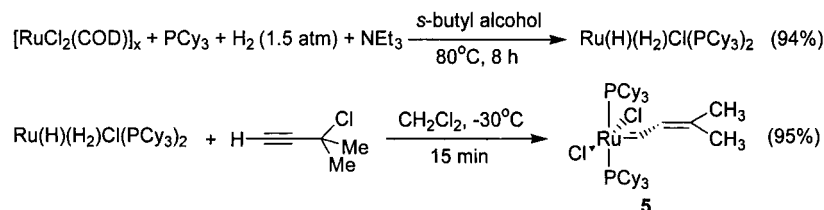
Although there were a number of ruthenium carbene complexes described in the literature by 1992, none of these were reported as being active for olefin metathesis. In 1992, the synthesis of complex **3** was described. The method is analogous to that used to make tungsten and titanium alkylidenes, namely reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ or $\text{RuCl}_2(\text{PPh}_3)_4$ with the strained olefin 3,3-diphenylcyclopropene [77] (Scheme 6.18).

Phosphine exchange reactions give the analogous bis-trialkylphosphine complexes such as **4** [78]. Calorimetric studies indicated that the exothermicity of the phosphine exchange scales well with various measurements of the electronic character of the phosphine, such as the basicity of the phosphine, and was not dependent on the steric bulk (Tolman cone angle) of the phosphine. Phosphine exchange of PPh_3 with PCy_3 (**3** to **4**) is exothermic by $6.5 \text{ kcal mol}^{-1}$ [79].

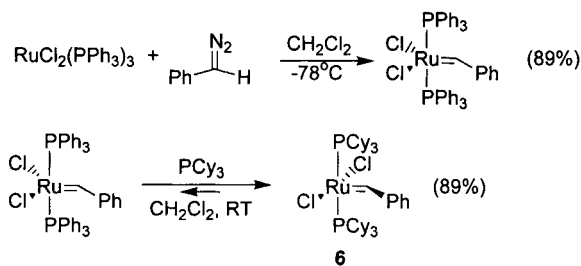
Another noteworthy synthesis of complexes of this type involves the insertion of a propargyl halide into the Ru-H bond of $\text{Ru}(\text{H})(\text{H}_2)\text{Cl}(\text{PR}_3)_2$ (Scheme 6.19),



Scheme 6.18 Synthesis of complexes **3** and **4**.



Scheme 6.19 Alternative synthesis of vinyl carbene complexes.

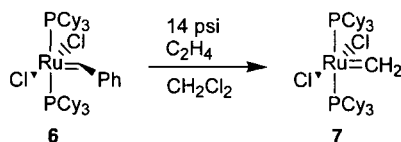
Scheme 6.20 Synthesis of complex **6**.

which has the advantages of inexpensive air-stable precursors and high yields [80]. This facile synthetic route is employed in the synthesis of complex **5** and derivatives.

Modification of the carbene is accomplished by reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with various alkyl- and aryldiazoalkane reagents (Scheme 6.20).

This procedure can be followed by phosphine exchange to give catalyst **6**. Complex **6** can be stirred under an atmosphere of ethylene to give quantitative yield of the methyldiene complex **7**, which was the first isolable and metathesis-active metal methyldiene complex reported in the literature [81] (Scheme 6.21). Complex **6** is the most widely used catalyst of this series, and is commonly referred to as the “Grubbs catalyst” or more recently as the “first-generation Grubbs catalyst”.

The geometry of these complexes ranges from distorted trigonal bipyramidal to distorted square pyramidal with Cl-Ru-Cl angles in the range of approximately 150° to 170° . The orientation of the carbene with respect to the P-Ru-P plane is also variable. In the PPh_3 complexes the carbene moiety is approximately coplanar (off by about 9°) with the P-Ru-P plane, and for the complexes of bulky phosphines, the carbene is twisted approximately normal to the P-Ru-P plane. This is witnessed in the ^1H NMR spectra by the multiplicity of the H_a signal. The P-H coupling constant is high (~ 10 Hz) when H_a is close to the P-Ru-P plane and low (~ 0 Hz) when twisted normal to this plane. Thus H_a displays a pair of overlapping triplets for **3** and a singlet for **6** [77, 78, 80]. Interestingly, another complex of this type exists in the solid state with the carbene moiety twisted approximately 45° from the P-Ru-P plane, suggesting that the barrier to rotation about the metal carbene bond is not prohibitively high [82]. The carbene unit is considered a neutral L-type ligand, in contrast to Schrock carbenes. The electronic structure could be considered intermediate between Schrock and Fischer carbenes. This treatment of the carbene renders the ruthenium as Ru(II), although it is also shown as Ru(IV) in some cases [83].

Scheme 6.21 Preparation of methyldiene complex **7**.

These complexes display varying degrees of stability, but the general trends are that solutions of the complexes are not rapidly decomposed by alcohols or water. Solutions of these complexes may be prepared on the bench-top in reagent-grade solvents and will slowly decompose over a matter of hours by oxidation to a green material. The solid complexes are stable over a period of weeks in air and indefinitely in a dry-box. The PCy₃ complexes are more stable than the PPh₃ complexes. Benzyldiene **6** is stable indefinitely in air in the solid state and in inert solution at temperatures up to 60 °C [77, 78, 80].

6.5.2.2 Use in ADMET

The metathesis activities of these complexes also vary throughout the series. The PPh₃ complexes, such as **3**, are active only for ROMP of strained cyclic olefins. However, the PCy₃ analogues are active towards acyclic olefins, and thus promote ADMET [84]. The importance of the identity of the carbene is illustrated by the difference between complexes **5** and **6**, in that **5** initiates very slowly, and typically only a small amount (~10%) of the vinyl carbene is converted into the alkylidene. Thus, complex **5** is a poor ADMET catalyst at normal catalyst loading (0.1 to 1.0 mol%). Complex **6**, however, undergoes quantitative initiation of the initial benzyldiene and is an active ADMET catalyst, producing polymers with *M_n* of 25 to 35 kDa. This complex has been used to polymerize monomers containing ketones, alcohols, esters [49, 53], ethers [35], silyl chlorides, siloxanes [85], amides [55, 56], and carboxylic acids. However, thioethers are not tolerated [35]. The development of complex **6** greatly expanded the scope of ADMET by allowing polymerization of these functionalized dienes and by easing the requirement of absolute dryness of monomers required for polymerization with **1** or **2**. Some desirable ADMET monomers are non-distillable liquids, and ADMET with **6** proceeds normally after simply heating the purified monomer under vacuum in the liquid state overnight to remove oxygen [53].

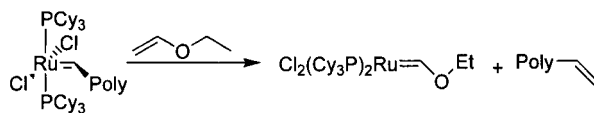
The kinetics of ADMET with complex **6** were compared to those of complex **2** by measuring the volume of ethylene liberated from ADMET reactions over time [35]. Obtaining an approximate second order rate constant from the DP versus time curves, it was found that molybdenum complex **2** polymerizes 1,9-decadiene 24 times faster than ruthenium complex **6** (Tab. 6.1).

The polymerization of ether and thioether monomers was also studied, and it was found that the rate of polymerization was a great deal slower with the functionalized monomers. The number of methylene units between the olefin and the heteroatom greatly affected the rates observed, giving credence to the chelation effect shown in Fig. 6.1. In addition, catalyst **2** polymerizes 1,5-hexadiene, whereas catalyst **6** mainly cyclizes the metathesis dimer to cyclo-1,5-octadiene. At this point there is no clear explanation for this result, and, furthermore, the reason that the COD generated did not undergo ROMP in these reactions is unclear. The data from these experiments clearly shows that Lewis basic functionality retards the rate of metathesis with complex **6** more than with complex **2**, although **6** is clearly the more functional group-tolerant complex overall [35].

Tab. 6.1 Relative rates of ADMET at 25 °C [6].

Monomer	Complex 2 ^{a)}	Complex 6 ^{a)}
1,9-decadiene	24	1.0
di-4-pentenyl ether	12	0.06
di-4-pentenyl ether	15	0.1
di-4-pentenyl sulfide	2	0
di-5-hexenyl sulfide	13	0
1,5-hexadiene	41	Cyclization

a) Expressed as second order rate constants relative to 1,9-decadiene with complex 6 “(1×10^{-4} L mol⁻¹s⁻¹)”.

**Scheme 6.22** Reaction of ruthenium carbenes with ethyl vinyl ether.

These ruthenium complexes react rapidly and quantitatively with ethyl vinyl ether to form a Fischer carbene that is only weakly metathesis active at elevated temperatures [86, 87]. This property can be employed to end-cap ROMP and ADMET polymers and to ensure that there are no polymeric ruthenium alkylidenes present. Since ruthenium alkylidenes are relatively robust complexes they could survive workup procedures, although experimental evidence has yet to confirm this notion. Treatment of an ADMET polymer with ethyl vinyl ether gives the polymer well-defined terminal olefinic endgroups and should prevent backbiting metathesis upon dilution of the polymer (Scheme 6.22).

6.5.3

Second-Generation Grubbs Catalysts: RuCl₂(NHC)(PR₃)CHR₁

6.5.3.1 Synthesis and Activity

The next breakthrough in catalyst synthesis was the incorporation of the N-heterocyclic carbene (NHC) ligands into these complexes. These ligands are referred to as phosphine mimics, and in many cases they can be directly substituted for phosphines in catalysts with retention or increases in catalytic activity. Arduengo and co-workers pioneered the development of these ligands by the demonstration that carbenes of this type could be generated and in some cases are remarkably stable, although sensitive to air and especially moisture [88–91]. In contrast to most organic carbenes, N-heterocyclic carbenes are ground state singlets and are similar in electronic structure to the CF₂ carbene [92]. The energy difference between the singlet and triplet states for a typical N-heterocyclic carbene has been calculated to be 79.4 kcal mol⁻¹, twice that of the CF₂ carbene. The electronic structure of the NHC is not completely understood, and there is debate in the lit-

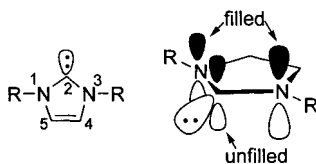
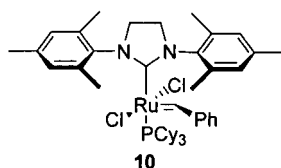
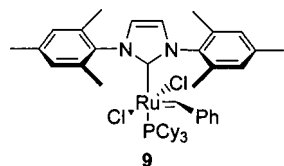
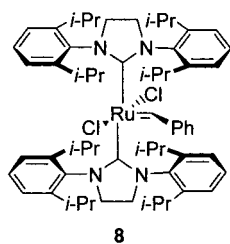


Fig. 6.3 N-Heterocyclic carbenes: numbering and crude orbital picture neglecting C4 and C5.

erature as to the role of conjugation, but it is commonly accepted that interaction of the two filled α -N(π) orbitals with the unfilled C(π) orbital renders the energy of the C(π) orbital quite high. The high energy of the C(π) orbital presumably leads to the observed singlet ground state and the tendency of the NHC to form σ bonds with metals (Fig. 6.3). Saturation of the carbon-carbon double bond (C4–C5 in Fig. 6.3) leads to a lower singlet-triplet gap, however, which seems to contradict the former statement. There is even apparent controversy over the nomenclature; the form used in the majority of the metathesis literature will be used herein [92].

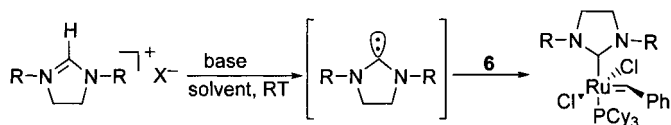
Many groups have used NHC ligands in complexes with almost every transition metal and many other elements. The carbene unit as a ligand in metal complexes is very σ -donating and very poorly π -accepting. These complexes are less π -accepting than PMe_3 and even nitriles as judged by *trans*-CO stretching frequencies in Ni complexes. They are also very nucleophilic and basic. The $\text{p}K_{\text{a}}$ of the conjugate acid has been measured to be 24 in $\text{DMSO}-d_6$, and is therefore one of the strongest known neutral bases (phosphazenes are more basic than NHCs, however) [92]. Since the metathesis activity of the bis-phosphine ruthenium metathesis catalysts increases with the σ -donating properties of the phosphines, the use of NHC ligands was a quite logical extension. Nolan et al. determined that for Cp^*RuClL (Cp^* =pentamethylcyclopentadienyl) complexes the substitution $\text{L}=\text{PCy}_3$ to $\text{L}=1,3$ -dimesitylimidazol-2-ylidene (IMes) is exothermic by 5 kcal mol^{-1} , demonstrating the strong bonding of this carbene to the ruthenium atom [93]. Herrmann and co-workers have contributed greatly to the NHC field in general and reported the first metathesis catalysts containing NHC ligands, including complex **8** [94]. These complexes showed little improvement over complex **6** in metathesis reactions, but the mixed ligand complexes of the type $\text{RuCl}_2(\text{NHC})(\text{PR}_3)\text{CHR}_1$ have shown enormous benefits in activity and stability compared to **6**. The Nolan group reported the mixed ligand complex **9** [93, 95], which contains the 1,3-dimesitylimidazol-2-ylidene (IMes) ligand. The Grubbs group independently reported the saturated analogue, complex **10** [96], which contains the 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (SIMes) ligand. This saturated analog of the IMes ligand was expected to be more basic than IMes due to the reduced conjugation through the NHC ring and hence a better ligand than IMes for olefin metathesis with these complexes. A large number of synthetic variations have since been reported for these ligands [97], and although activity profiles throughout this series of complexes are not straightforward, complex **10** is generally the most active and popular complex of this type.

Although the NHC ligands are carbenes, the metal-carbon bond of the NHC is completely different than that of the ruthenium benzylidene bond, displayed in

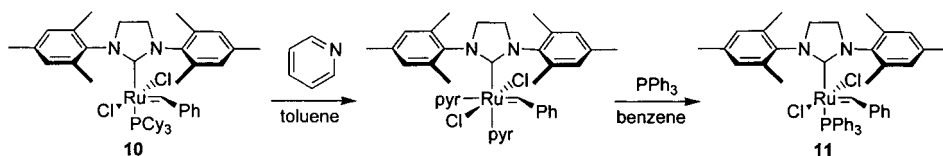


part by the bond lengths. The distance of the ruthenium NHC bond in complex **9** is quite long at 2.069 Å, whereas the ruthenium- C_{α} bond length is the usual 1.841 Å [93]. This longer, and therefore weaker, bond to the NHC carbon supports the notion that the NHC ligand is a very weak $d(\pi)$ acceptor and highlights the very different nature of the two metal-carbon bonds of these complexes. The Cl-Ru-Cl bond angles in these complexes are approximately 170° and the carbene fragments are perpendicular to the $C_{\text{NHC}}\text{-Ru-P}$ plane.

There are a number of methods to synthesize NHC ligands and complexes. The preferred method in the context of synthesizing ruthenium olefin metathesis catalysts involves generation of the free carbene by treatment of a ligand precursor imidazolium salt with a base to generate the free carbene, followed by addition to a solution of complex **6** (Scheme 6.23). This process can achieve high yields (>90%). In contrast to complex **6**, complex **10** can be purified by column chromatography on neutral silica, to give very pure complex **10** in >70% yield [98].



Scheme 6.23 General synthesis of NHC metathesis catalysts.



Scheme 6.24 Phosphine exchange via bis-pyridine adduct.

Another useful synthetic manipulation of NHC complexes is phosphine exchange via the bis-pyridine adduct. Thus complex **11** can be synthesized by reaction of complex **10** with an excess of pyridine, isolation of the bis-pyridine adduct, and reaction of this complex with PPh_3 [99] (Scheme 6.24).

All of these mixed-ligand NHC-phosphine complexes are active to all modes of olefin metathesis. Complex **10** has been used extensively for ADMET. The ADMET of dienes with complex **10** gives polymers of higher molecular weight than those from complex **6**. For the ADMET of 1,9-decadiene, molecular weights of 60–70 kDa can be easily achieved. Additionally, this complex has allowed solution ADMET polymerization of monomers containing amino acid groups [55]. Monomers containing multiple amino acid residues are polymerized to molecular weights of up to 30 kDa. The use of THF as solvent is crucial to the successful polymerization of some of these highly functionalized monomers [56].

The kinetics of polymerization of 1,9-decadiene by complex **6** and complex **10** were compared by measuring the volume of ethylene liberated over time. It was found that complex **10** catalyzed ADMET up to six times faster than complex **6** at temperatures of 45 to 75 °C, but complex **6** was the faster catalyst at 30 °C. Additionally, complex **10** displayed a very conspicuous induction period that was not present for catalyst **6**. It was also apparent that complex **10** is stable over at least a period of hours at 75 °C in the presence of dienes, whereas complex **6** rapidly decomposes at this temperature [100].

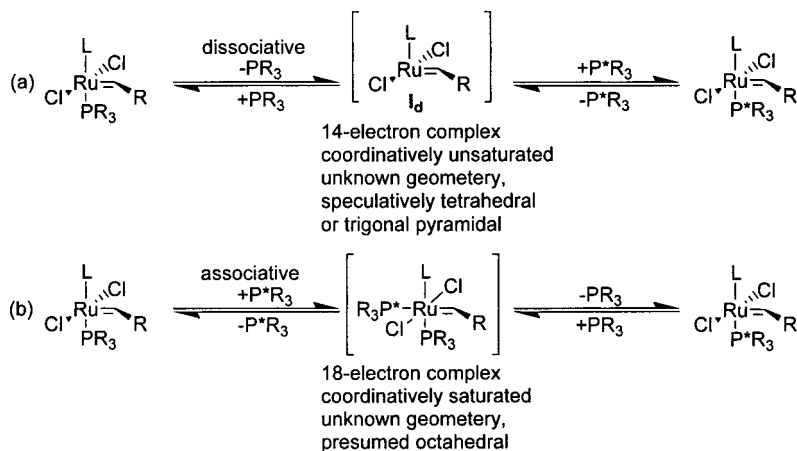
6.6

Mechanism of ADMET with Grubbs Catalysts

6.6.1

Role of the Phosphine Ligand: $\text{RuCl}_2(\text{PR}_3)(\text{L})\text{CHR}_1$

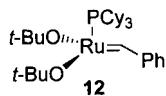
The identity of the phosphine ligand is critical to the metathesis activity of these ruthenium catalysts. Even subtle substitution of cyclopentyl groups for cyclohexyl groups or substitution of one phenyl group for a cyclohexyl group of PCy_3 gives catalysts with dramatically different olefin metathesis activities. Based on activity data alone, the exact nature of the role of the phosphine is unclear, though. For the first generation catalyst series, the more basic phosphines were thought to stabilize the formal Ru(IV) metallacyclobutane intermediate, and thus promote metathesis. Based on a detailed study carried out on the methylenide catalyst **7** it was



Scheme 6.25 Dissociative (a) and associative (b) ligand exchange mechanisms.

also believed that a mono-phosphine complex was responsible for more than 95% of observed metathesis activity. It was therefore suggested that more sterically bulky phosphines promote metathesis by promoting phosphine dissociation [36]. Magnetization transfer ^{31}P NMR experiments established that degenerate phosphine exchange (phosphine dissociation and rebinding in the absence of olefin) for the whole family of complexes is dissociative rather than associative. This was somewhat of a counter-intuitive result, since the intermediate derived from dissociation of a phosphine ligand, I_d , is a coordinatively unsaturated, 14-electron species, whereas the intermediate expected from associative ligand exchange is a presumably octahedral 18-electron complex (Scheme 6.25). Intermediate I_d has not been spectroscopically observed [101].

In support of the existence of I_d , the 14-electron complex **12** and partially fluorinated analogues have been isolated and characterized [102]. Complex **12** adopts a slightly distorted trigonal pyramidal geometry in the solid state, with a planar P-Ru-C $_{\alpha}$ -H $_{\alpha}$ unit (C $_{\alpha}$ -H $_{\alpha}$ refers to the carbene carbon and proton). Thus, the carbene has rotated approximately 90° relative to the parent complex **6**. No agostic interactions were present. This complex is much more sterically bulky than I_d , but the structure may provide some insight into the nature of this highly metathesis-active intermediate. The structural similarity of **12** to the Schrock catalysts **1** and **2** is particularly intriguing.



Tab. 6.2 Phosphine exchange rates for various ruthenium complexes in toluene- d_8 at 80 °C [101].

Complex ^{a)}	Exchange rate [s^{-1}]
6	9.6
[Ru]=CHEt	19.4
5	0.33
10	0.13
11	7.5

a) [Ru] = RuCl₂(PCy₃)₂.

To confirm that a dissociative ligand exchange mechanism is in operation, the kinetics of the rapid reaction of these complexes with ethyl vinyl ether was studied by NMR and UV/VIS spectroscopies. The results were in complete agreement with a dissociative ligand exchange mechanism for all complexes in this series, with the possible exception of the diiodo derivatives [101].

The results of the phosphine dissociation experiments for the various ruthenium complexes were surprising in that the second-generation catalysts exchange phosphine ligands slower than the first-generation analogs (Tab. 6.2).

At first the unprecedented activity of the second-generation catalysts was thought to be a result of faster phosphine dissociation [95]. This result indicated that the phosphine dissociation kinetics as well as the metathesis activity of the resulting 14-electron intermediate must be considered to rationalize the activity of these catalysts. Interestingly, returning to PPh₃ is valuable for the NHC complexes, in that the phosphine exchange rate for complex **11** is almost that of complex **6** [101].

The effects of this kinetic situation were clearly demonstrated in the context of ADMET. In DP versus time curves (Fig. 6.4) for the ADMET of 1,9-decadiene with complexes **6** and **10** a conspicuous induction period is witnessed for **10** that is absent for **6**.

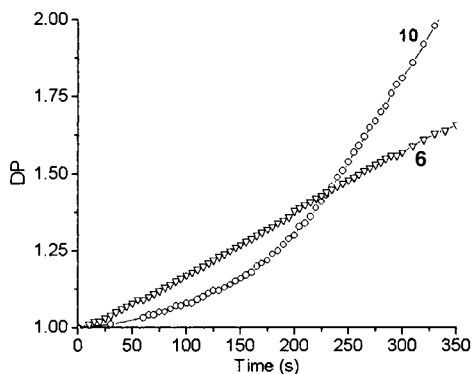


Fig. 6.4 DP vs. time data at low conversion (monomer to dimer) for ADMET of 1,9-decadiene at 45 °C showing the induction period of catalyst **10**. (Reprinted with permission from Lehman, Jr., S. E., Wagener, K. B., *Macromolecules* **2002**, 35, 48–53.)

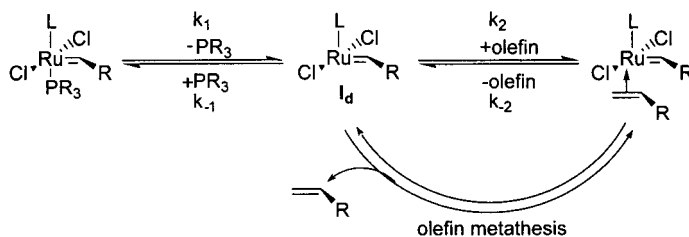
It was proposed that during the induction period phosphine is slowly dissociating from the complex to form I_d , and the concentration of I_d finally reaches a quasi-steady state when the rate of ADMET is observed to be constant. In contrast, the more rapid phosphine dissociation of complex **6** results in the observation of a constant maximum ADMET rate from the first data point onward. Once the equilibrium state of phosphine dissociation is reached, complex **10** promotes ADMET twice as fast as **6** at 45 °C due to the higher reactivity of the NHC-derived I_d compared to the phosphine-ligated I_d resulting from complex **6**.

6.6.2

Role of the L Ligand: $RuCl_2(PR_3)(L)CHR_1$

The kinetic data from phosphine dissociation studies and reaction with ethyl vinyl ether fit the classical dissociative exchange catalysis model very well [101]. Examination of this model leads to the conclusion that there are two main factors controlling the activity of these catalysts: the rate of phosphine dissociation and the metathesis activity of the phosphine-dissociated species (Scheme 6.26).

Thus the ratio of the rates of phosphine binding and olefin binding to I_d is key to rationalizing the reactivity of these complexes, assuming that olefin binding is the rate limiting step in metathesis with these complexes. This ratio, k_{-1}/k_2 , is estimable from the experiment described above; the lower this ratio, the higher the observed metathesis activity (Tab. 6.3). The results confirm that the high activity of the second-generation Grubbs catalyst is due to the propensity of the I_d to bind olefins over phosphine [101].

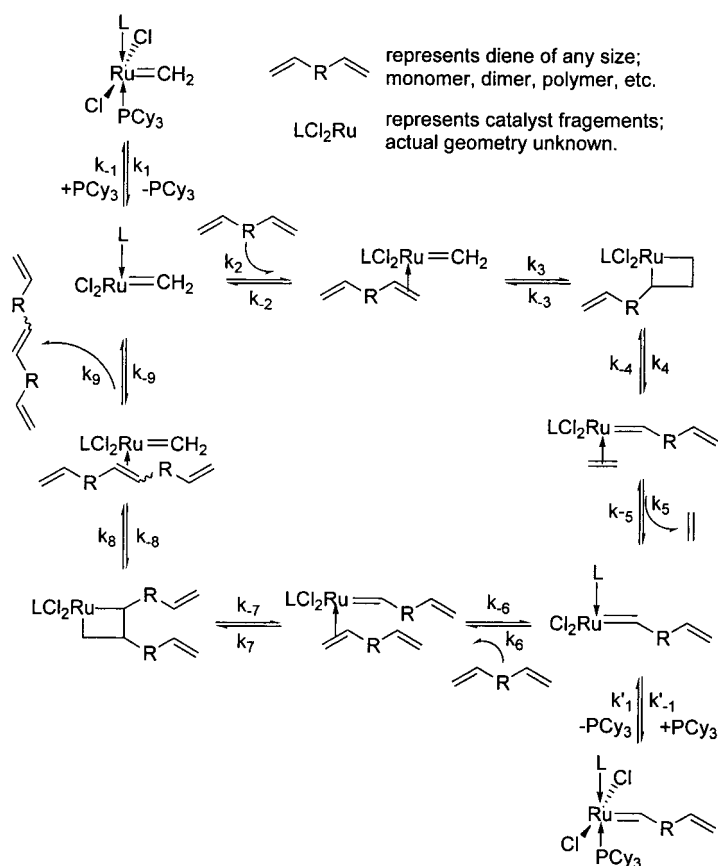


Scheme 6.26 Dissociative phosphine-olefin exchange model for metathesis.

Tab. 6.3 Estimated k_{-1}/k_2 values [101].

Complex [1]	Temperature [°C]	k_{-1}/k_2
6	50	13 000
5	50	810
10	50	1.25
11	25	2.3

This phenomenon must be due to the nature of the L ligand *trans* to the labile phosphine (the L ligand is a phosphine for complexes **5** and **6** and an NHC ligand for complexes **10** and **11**) and can be rationalized by consideration of the greater π -acidity of trialkylphosphines over the NHC ligands. The weaker π -acidity of the NHC ligand renders the π -backbonding interaction of the ruthenium-phosphine bond stronger in complex **10** compared to complex **6**, for example. The stronger ruthenium-phosphine bond can explain the slower phosphine dissociation rate of the NHC complexes versus the bis-phosphine complexes, such as **6**, which would have weaker Ru-P π -backbonding interactions due to competition by two phosphines for the same ruthenium orbital, presumably. By the same token, the olefin-ruthenium back-bonding would be expected to be stronger for the NHC complexes due to the lack of competition for the Ru(π) electron density by phosphine. The stabilization energy difference of π -backbonding between olefin-binding and phosphine-binding *could* be greater for NHC complexes than for the bis-



Scheme 6.27 Revised ADMET mechanism for Grubbs catalysts [100].

phosphine complexes, due to more orbital mixing with the Ru component when not partially donated to a phosphine. This effect could be responsible for the greater affinity of the 14-electron intermediates derived from NHC complexes to bind olefins over phosphines. This cursory explanation is speculative, although theoretical calculations could support the notion or shed light onto other factors controlling the ligand binding.

These data in total have led to the revising of the ADMET mechanism with ruthenium-based catalysts to include the very important aspect of phosphine dissociation (Scheme 6.27). In this mechanism k_3 , k_4 , k_7 , and k_8 are assumed to be very fast, such that the dissociative olefin-phosphine exchange is the rate-determining process [100].

6.6.3

Role of the Carbene: the Special Case of the Methylidene

In addition to the effects of the phosphine and the L ligand, the carbene fragment has an impact on the metathesis activity of these complexes. As established above, phosphine dissociation can be the rate-limiting step in the initiation (first turnover), especially for the NHC complexes, and thus it is difficult to directly compare the metathesis activity of different carbenes in the absence of the influence of phosphine dissociation. One obvious trend is that the methylidenes are particularly less reactive than other carbenes for this catalyst series. This has great impact on the ADMET reaction since the methylidene is involved in each turnover.

Phosphine dissociation is not rate limiting for the first-generation complexes [101], and as such some insight is gained by examining the initiation rates for these complexes. Selected results are given in Tabs. 6.4 and 6.5.

For reaction of the various ruthenium carbenes with either the terminal olefin 1-hexene [103] or ethyl vinyl ether [101], the rate of reaction increases in the order methylidene < vinyl carbene < benzylidene < alkylidene. The differences in rates were quite significant, especially for the methylidene, which is quite slow to initiate. The data also show that internal olefins are slower to react, but only by about an order of magnitude; the *cis* isomers being more readily metathesized than the

Tab. 6.4 Kinetics of reaction of olefins with ruthenium carbenes as monitored by NMR spectroscopy [103].

Temperature [°C]	Olefin	Carbene ^{a)}	Relative rate
7	1-hexene	[Ru]=CHPh (6)	1.00
7	1-hexene	[Ru]=CHEt	5.52
35	1-hexene	[Ru]=CHPh (6)	~ 8.5
35	1-hexene	[Ru]=CH ₂ (7)	~ 0.4
35	<i>cis</i> -3-hexene	[Ru]=CHPh (6)	0.51
35	<i>trans</i> -3-hexene	[Ru]=CHPh (6)	0.20

a) [Ru] = RuCl₂(PCy₃)₂.

Tab. 6.5 Initiation kinetics as measured by reaction of the carbene with ethyl vinyl ether [101].

Temperature [$^{\circ}\text{C}$]	Carbene ^{a)}	Relative rate
10	[Ru]=CHPh (6)	1.0
40	[Ru]=CH ₂ (7)	0.85
0	[Ru]=CH ₂ Et	0.54
25	[Ru]=CHCH=C(CH ₃) ₂ (5)	1.0
35	[Ru] [*] =CHPh	0.46
10	[Ru] ^{**} =CHPh	3.3
85	[Ru] [*] =CH ₂	<1.0

a) [Ru] = RuCl₂(PCy₃)₂; [Ru]^{*} = RuCl₂(PCy₃)(SIMes); [Ru]^{**} = RuCl₂(PPh₃)(SIMes).

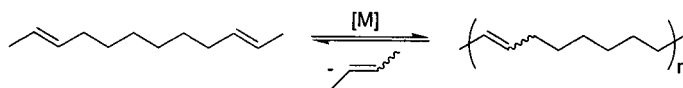
trans by a factor of about two. The reasons for these trends are both steric and electronic in nature. The alkylidene moiety, being electron donating and somewhat sterically bulky, probably assists the dissociation of a phosphine ligand and stabilizes the formal Ru(IV) metallacycle intermediate, thus increasing the rate of reaction with an olefin.

It is notable that the methylenes, especially the second-generation methyldene, are relatively unreactive towards metathesis. In fact, the second-generation methyldene complex polymerizes cyclooctadiene by ROMP 4 orders of magnitude slower than benzylidene **10** [101]. Thus, the unique properties of the methyldene complex discussed above are even more apparent for the second-generation catalyst series, due to the extremely slow phosphine dissociation of the methyldene complexes.

These results indicate that the methyldene complex is the “bottleneck” in the ADMET reaction with Grubbs catalysts, which suggests that performing the ADMET reaction on internal olefins may be beneficial. For example, ADMET with 2,10-dodecadiene versus 1,9-decadiene would completely avoid formation of the methyldene and removal of 2-butene would be the driving force of the reaction (Scheme 6.28).

Ruthenium alkylidenes would be the only propagating species. This theory has yet to be tested, however, because the rates of reaction of the benzylidene with internal olefins are lower than that with 1-hexene (Tab. 6.4). With the advent of the second-generation catalysts, however, the benefit of avoiding the methyldene may outweigh the reduced rate of reaction with internal olefins.

The other strategy to counteract the slow kinetics of the methyldene is to modify the phosphine in order to make the methyldene phosphine more labile. This

**Scheme 6.28** ADMET of internal dienes.

is easily done with catalyst **11**. ADMET with catalyst **11** could give higher molecular weight polymers than that with catalyst **10** because the methyldiene **I_d** generated from **11** is less likely to be trapped by PPh₃ than that from **10** with PCy₃, if it follows the same trend as the benzyldienes shown in Tab. 6.5 [101]. This question is currently being probed.

It should be mentioned that although the methyldiene displays anomalous kinetic behavior, complex **10** is active for ADMET and produces higher molecular weight polymers than **6**, in many cases. In other cases, the two complexes produce polymers of similar molecular weights. This observation was recently reported for the ADMET of phosphazene-containing monomers, which could be due to the relative inactivity of the methyldiene [104].

6.6.4

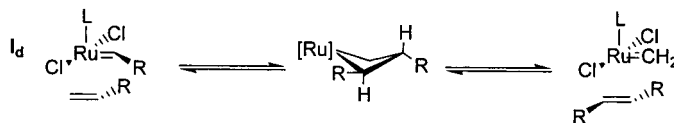
Stereochemical Aspects of ADMET

The stereochemical outcome of the metathesis reaction in ADMET with Grubbs catalysts determines the ratio of *cis* and *trans* olefins in the polymer, which affects the physical properties of the polymer. In addition, consideration of the formation of metallacyclobutane shows that a great majority of the metathesis events in an ADMET reaction are non-productive, and it is the occurrence of the less favored pathways that cause productive ADMET.

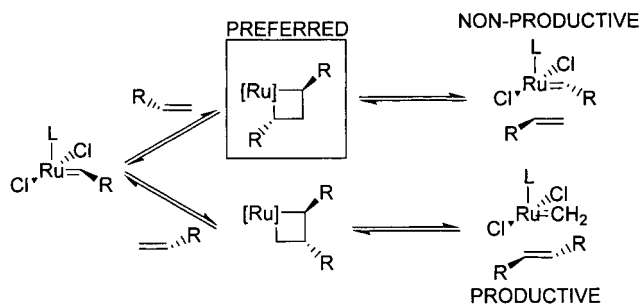
The *cis* to *trans* ratio of most ADMET polymers is approximately 3:7 to 1:4 after long reaction times. The preference for *trans* olefin formation is easily rationalized by consideration of both approach of the olefin to the metal center for productive chain extension and the conformation of the resulting metallacyclobutane (Scheme 6.29).

The *trans* microstructure is not only a reflection of the kinetic product rationalized by the metallacyclobutane conformation and approach of the olefin to the metal carbene, but is also a reflection of the eventual thermodynamic preference for *trans* olefins resulting from *trans*-metathesis olefin equilibration (see Scheme 6.11).

It has been demonstrated, however, that the kinetic product of reaction of **6** or the propylidene analog with a terminal olefin is the alkylidene, and not the methyldiene. This preference could be explained by the greater stabilization of the formal Ru(IV) metallacycle by the electron-donating alkyl groups at the α -position compared to the β -position [103]. However, the α,β -disubstituted metallacycle is required for productive metathesis (Scheme 6.30).



Scheme 6.29 Stereochemical rationalization of the preference for *trans* olefins in ADMET with Grubbs catalysts.



Scheme 6.30 Stereochemical preference of the α,α' -disubstituted metallacyclobutane.

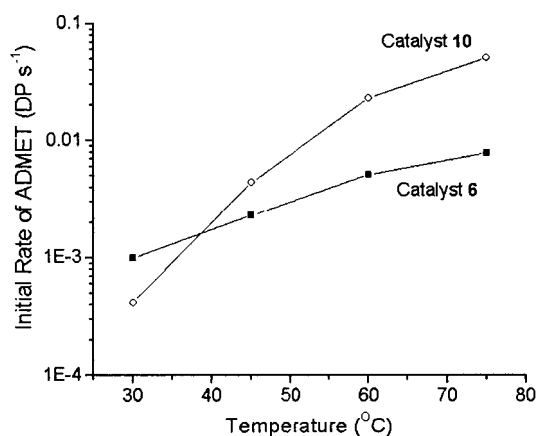


Fig. 6.5 Temperature dependence of initial rate of ADMET of 1,9-decadiene. (Reprinted with permission from Lehman, Jr., S. E., Wagener, K. B., *Macromolecules* **2002**, 35, 48–53.)

This preference is not energetic enough to prohibit ADMET, however, and increasing the temperature of the reaction will reduce the preference for the α,α' -disubstituted olefins. This may be one factor in the temperature dependence of the rate of ADMET of 1,9-decadiene. The Arrhenius plot for the polymerization of 1,9-decadiene with complex **6** or complex **10** is not linear (Fig. 6.5), especially for complex **10**, indicating that there are more than one temperature-dependent processes occurring, which probably include decomposition, phosphine dissociation, inherent metathesis activities of the I_d species, and ratio of productive and non-productive metathesis.

6.6.5

Catalyst Decomposition

The exact mechanism of catalyst decomposition for these complexes is not rigorously known. Several general points need to be described, however. First, the decomposition of the ruthenium carbenes is second order in catalyst. Thermolytic half-lives for some of these complexes have been measured and some of these data is tabulated in Tab. 6.6.

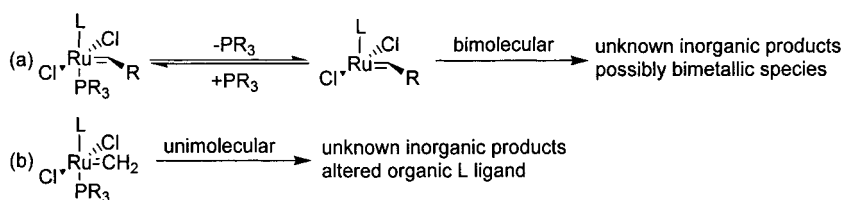
Second, the decomposition rate is retarded in the presence of excess phosphine. This behavior indicates that it is the phosphine-dissociated species **I_d** that undergoes the majority of the decomposition, presumably by some kind of dimerization reaction to produce unknown inorganic products [105] (Scheme 6.31). This also indicates that the rate of phosphine dissociation is critical to the rate of decomposition, consistent with the observation that the second-generation catalysts are more stable than the first [96].

Again, the methyldiene complex shows different behavior than the other carbenes. The decomposition of the methyldiene is not affected by the presence of excess phosphine and is first order in catalyst. The decomposition in this case appears to be due to activation of C-H bonds in the L ligand.

Tab. 6.6 Thermolytic half-lives at 55 °C in benzene-*d*₆ for selected complexes [96, 105].

Complex ^{a)}	Half-life
6	8 d
7	40 min
[Ru]=CHEt	8 h
[Ru]*=CH ₂	6 h

a) [Ru] = RuCl₂(PCy₃)₂; [Ru]* = RuCl₂(PCy₃)(SIMes).



Scheme 6.31 Decomposition processes: (a) general carbene (b) methyldiene complex.

6.7

Experimental Considerations for ADMET

6.7.1

The Ideal Case: Bulk ADMET with High Vacuum

In contrast to many chain polymerizations catalyzed by transition metal complexes, the experimental procedure for ADMET is relatively straightforward. The elaborate glassware used in the early days of ADMET to capture and identify condensate gases has mostly given way to normal laboratory glassware. An ideal ADMET polymerization would proceed as follows. A non-volatile liquid monomer and catalyst are combined in a round bottom flask or Schlenk tube containing a magnetic stirbar either in a drybox or using standard Schlenk technique. This flask is equipped with a Teflon high vacuum valve and a suitable joint to connect the apparatus to a vacuum line. With stirring, the vessel is slowly exposed to vacuum in steps or by using a valve that can easily be metered. It is of great importance to use care when applying the vacuum to prevent splashing of the monomer up onto the sides of the flask, as the liberation of ethylene and rapid degassing of dissolved inert gas can be very vigorous. As the vacuum is increased, the temperature of the vessel is raised to the desired temperature. The viscosity of the material increases as the reaction proceeds, but ideally slow magnetic stirring may be maintained for the polymer melt. The effect of ultimate vacuum on molecular weight has not been systematically studied, but typically an ultimate vacuum of 1–3 mtorr is easily obtained on a well-sealed vacuum line with a liquid nitrogen trap with either a direct-drive or belt-drive vacuum pump. The use of an oil diffusion pump can achieve a higher ultimate vacuum, typically by about an order of magnitude. In any case, once high vacuum is reached it is maintained for typically five days. The polymer is then removed from the vacuum line, quenched if desired with an appropriate reagent or by exposing to air in the case of Group VI catalysts, and either passed through a silica column to remove catalyst residues, or, if the polymer is a solid at room temperature, precipitated from a good solvent into a poor solvent such as acidic (1 M HCl) methanol to give the polymer as a solid.

6.7.2

The Ideal Case: Bulk ADMET with Carrier Gas

ADMET may also be conducted by stirring a bulk monomer under an inert gas flow, thus exploiting the natural volatility of ethylene to shift the equilibrium towards high polymer. Although this method is fundamentally not as efficient at removing ethylene, it has the advantage of experimental ease and, in some cases, can give polymers of similar molecular weight as those polymerized under vacuum. In this case, catalyst and non-volatile liquid monomer are added to a three-neck round bottom flask with a magnetic stirbar in a drybox or using Schlenk technique. The flask is equipped with two hose adapters with stopcocks, one of which is connected to an inert gas source, and the other is connected to an oil

bubbler. Inert gas is then passed through the vessel and out the bubbler at a convenient flow rate. Again, ethylene will be liberated and the viscosity of the reaction mixture will increase as a sign that ADMET is proceeding. Additional catalyst may be added as desired, and samples for GPC or other analyses may be conveniently taken if necessary. It may be advantageous to finish the reaction with vacuum to promote higher conversion. The reaction is worked up as above.

6.7.3

ADMET with Volatile Monomers

If a volatile monomer is used in an ADMET polymerization, a condenser should be used to return monomer vapor to the reaction mixture. The kinetics of step-growth polymerization dictate that the concentration of monomer falls very quickly to produce dimer, trimer, and so forth. Nevertheless, monomer will be present for some time after the start of the polymerization. If the monomer is particularly volatile, a dry ice-isopropanol condenser is useful. This can be constructed in any glass shop by attaching a cup-shaped cooling reservoir to a vacuum valve or other cylindrical glass tube with the required joints and valve. If the monomer is only slightly volatile, or the carrier gas method is used, a water-cooled condenser is sufficient to retain monomer in the flask, while allowing ethylene to escape.

6.7.4

Viscous or Solid Monomers or Polymers

Liquid ADMET monomers often become so viscous that magnetic stirring is impossible. There are several solutions to this. One is to attach a strong horseshoe or other magnet to a mechanical stirrer and rotate it very slowly under the vessel and temperature bath to slowly agitate the polymer melt. Another solution is to use a high viscosity mechanical stirrer if the polymer is a viscous melt. Vacuum adapters for the stirring shaft are available, so that the vacuum method may be used with mechanical stirrers.

If the polymer solidifies upon polymerization, solvent may be added to disperse the polymer. If the monomer is a solid, solvent may be used from the beginning of the reaction. Solvent may be added through a Teflon valve or into an extra neck containing a septum via syringe or cannula. Schlenk technique should be used throughout. A vacuum may then be periodically applied. Ethylene and solvent will both distill out upon application of high vacuum. A moderate vacuum (30 torr, for example) may also be used with a high boiling solvent and water-cooled condenser to remove ethylene and retain most of the solvent in the vessel. The carrier gas method, with no vacuum, also works in concentrated solution.

It is recommended that the least amount of solvent required to disperse the solvent be used to avoid formation of cyclic oligomers. Also, if applying vacuum to a solution ADMET polymerization, the vacuum should be applied very carefully to prevent bumping.

It has recently been demonstrated that ADMET occurs in the solid state. If the ADMET of 1,9-decadiene is carried out at temperatures below 60 °C, the polyoctenamer will solidify after an average DP of about 5 is reached. Using the carrier gas method, ADMET continues in this solid for days as proven by GPC analysis. In some cases molecular weights of greater than 70 kDa with complex **10** have been observed by this method. It is not a general method, however, and the scope and limitations are still being explored [106].

6.8

Conclusions and Outlook

In conclusion, the expanded scope of ADMET is largely due to the development of well-defined late-transition metal catalysts that are functional group-tolerant and easy to handle and synthesize. The potential for ADMET is very great, in that it is a mild method of forming useful linear condensation polymers and copolymers. The application of ADMET in modeling polyolefins and other polymers is just being discovered, and this aspect of ADMET is expected to further the understanding of these enormously important polymers.

Catalyst synthesis is also progressing at a rapid rate, which will allow ADMET to be carried out under even simpler conditions and with more and more functionalized monomers. New catalysts that display both higher activity and higher stability represent significant advances in catalyst design. Many potentially ADMET-active complexes were not discussed in this chapter, simply because they have not been used in ADMET chemistry. These include, among others, the styrenyl ether-based complexes developed by Hoveyda [98, 107] and two classes of catalysts developed by Grubbs: bimetallic complexes [108] and salicylaldimine-ligated ruthenium complexes [109]. Metathesis polymerization in general is expected to be an enormously important field of active research and development in the future, both academically and industrially, which has and will attract many talented young minds.

6.9

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7

Transition Metal-Catalyzed Polymerization in Aqueous Systems

STEFAN MECKING and JÉRÔME P. CLAVERIE

7.1

Introduction

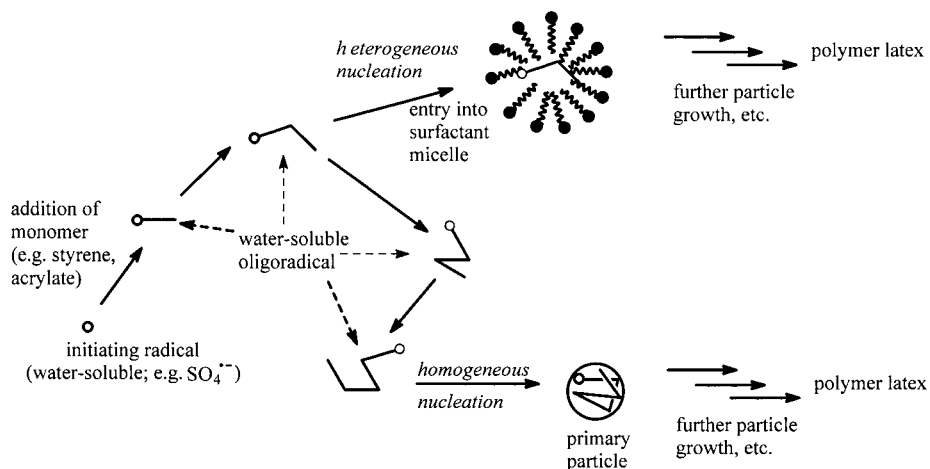
As a reaction medium for transition metal-catalyzed polymerizations, water will, most likely, not be the first choice. The extreme water sensitivity of Ziegler or Phillips catalysts is well known. However, carrying out polymerization reactions in aqueous systems offers unique advantages. Thus, traditional free-radical emulsion and suspension polymerization are carried out on a large scale industrially. A brief review of these established reactions demonstrates some specific properties of polymerizations in aqueous systems.

7.1.1

Traditional Free-Radical Polymerization in Aqueous Systems

In *emulsion* polymerization, polymer latexes are obtained as a product [1–4]. A polymer latex is a stable dispersion of polymer particles in the size range of ca. 50 to 1000 nm in a liquid medium, usually water. Latexes are also referred to as polymer dispersions, or polymer colloids. In such latexes, coagulation and precipitation of the polymer particles must be prevented. Stabilization can occur by different mechanisms: by electrostatic repulsion between the diffuse counterion layers surrounding particles (electrostatic stabilization), or by means of a layer of polymer on the particle surface that has a good miscibility with the dispersing medium and thus results in repulsion when the polymer layers of two approaching particles come into contact (steric stabilization). Electrostatic stabilization most often involves ionic low-molecular-weight surfactants adsorbed to the particle surface, whereas steric stabilization is usually brought about by water-soluble polymers adsorbed or covalently bound to the particle surface. The mechanism of free-radical emulsion polymerization is complex; nonetheless the following simplified considerations can illustrate underlying principles.

In a typical aqueous emulsion polymerization, a water-immiscible monomer is polymerized in the presence of a surfactant and a water-soluble initiator, such as potassium peroxydisulfate. A water-soluble radical, e.g. $\cdot\text{SO}_4^{2-}$ formed by thermal decomposition of the initiator, grows by addition of monomer dissolved in the



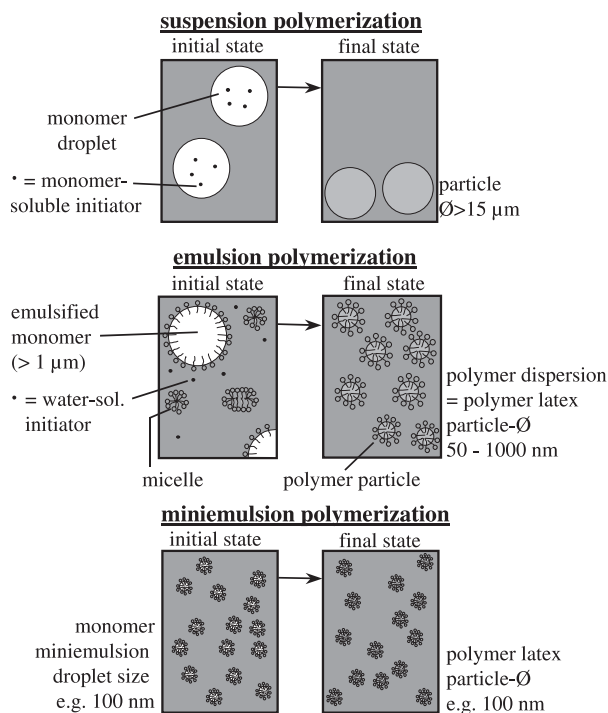
Scheme 7.1 Possible mechanisms of particle formation in free radical emulsion polymerization.

aqueous phase (also for “water-immiscible” monomers a small equilibrium concentration is present in the aqueous phase). Repeated monomer addition results in the formation of an oligomeric radical, which is initially water-soluble due to the incorporated sulfate moiety (Scheme 7.1). Upon reaching a certain critical chain length the growing radical chain becomes insoluble and collapses upon itself, thus nucleating a particle (“homogeneous nucleation”). This primary particle is stabilized by adsorption of surfactant, and further polymerization within the particle results in particle growth. Alternatively, a particle can be nucleated by the water-soluble oligomer entering a surfactant micelle prior to reaching its critical chain length (“heterogeneous micellar nucleation”).

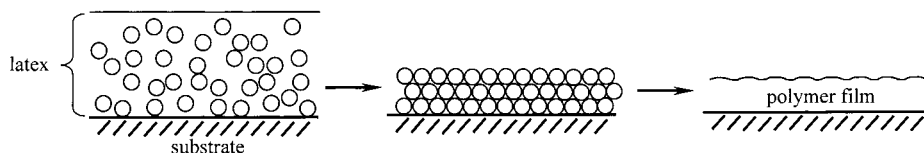
During emulsion polymerization the emulsified monomer droplets serve as a reservoir for monomer; however, polymerization usually does not occur in these droplets but in the formed polymer particles to which the monomers diffuses through the aqueous phase (Scheme 7.2).

Particular features of emulsion polymerization and polymer latexes are:

- After the polymerization, the polymer can be isolated by precipitation, but for many applications latexes are used as such. *Film* formation upon evaporation of the dispersing medium (Scheme 7.3) is a key step in many applications, and the fact that colloids are composed of submicron particles is advantageous in terms of forming continuous films.
- Water is *non-flammable* and *non-toxic*. This is advantageous not only in the polymerization process, but particularly in applications. By film formation from latexes, several million tons of water are evaporated into the atmosphere annually.
- Particle sizes can be controlled precisely in some cases (albeit usually involving trial and error). For example, monodisperse polystyrene latexes suitable as calibration standards can be prepared conveniently by emulsion polymerization.



Scheme 7.2 Free radical suspension, emulsion and miniemulsion polymerization.



Scheme 7.3 Film formation from a polymer latex upon evaporation of the dispersing medium.

- Due to the *kinetics* of the polymerization in small particles, emulsion polymerization allows for high polymerization rates and also high polymer molecular weights at the same time. This differs from bulk free-radical polymerization, where an increase in rate occurs at the expense of molecular weight and vice versa. However, this is obviously a feature of classical free-radical polymerization and must therefore not be considered further in the context of most transition metal-catalyzed polymerizations.
- Polymer latexes possess a *low viscosity* by comparison to a solution of the polymer in an organic solvent. During the polymerization process, this enables high yields per reactor volume. The latex products can be handled readily, e.g. they can be pumped. Also, many applications require a restricted viscosity. Polymer

dispersions with up to 70% solids content (that is the aqueous dispersion contains only 30 ca. wt.% water) are prepared commercially.

Aqueous dispersions of poly(vinyl acetate) and vinyl acetate-ethylene copolymers, homo- and copolymers of acrylic monomers, and styrene-butadiene copolymers are the most important types of polymer latexes today. Applications include paints, coatings, adhesives, paper manufacturing, leather manufacturing, textiles and other industries. In addition to emulsion polymerization, other aqueous free-radical polymerizations are applied on a large scale. In *suspension polymerization* a water-immiscible olefinic monomer is also polymerized. However, by contrast to emulsion polymerization a monomer-soluble initiator is employed, and usually no surfactant is added. Polymerization occurs in the monomer droplets, with kinetics similar to bulk polymerization. The particles obtained are much larger ($>15\text{ }\mu\text{m}$) than in emulsion polymerization, and they do not form stable latexes but precipitate during polymerization (Scheme 7.2).

Miniemulsion polymerization represents a special technique. Miniemulsions [5–7] can be prepared by subjecting a mixture of water, a surfactant, an organic phase and a small portion of a so-called hydrophobe to high shear. High shear results in the formation of very small droplets. These are stabilized towards Ostwald ripening [8] to larger droplets by the hydrophobe. Typical droplet sizes are in the range of 50 to 200 nm. In miniemulsion polymerization a miniemulsified monomer is polymerized to a latex, polymerization occurring in the droplets by contrast to emulsion polymerization. Ideally, the latex particles resemble replicas of the monomer droplets (Scheme 7.2). As the monomer must not diffuse through the aqueous phase, by contrast to emulsion polymerization, very hydrophobic water-insoluble monomers can also be polymerized with good rates. Not only water-insoluble initiators, but also water-soluble initiators can be utilized. In the latter case, entry into monomer droplets, which usually does not occur in emulsion polymerization, is favored by the very high number of small droplets. The advantages of miniemulsion polymerization are contrasted by the requirement of introducing high shear for miniemulsification, which is not routine on a larger scale. For this reason, industrial applications are limited to date [9].

In *dispersion polymerization*, by contrast to emulsion or suspension polymerization, a monomer which is soluble in the reaction medium is polymerized. In analogy to the aforementioned types of polymerization, an insoluble polymer is obtained. The reaction is carried out in the presence of non-ionic surfactants or soluble polymers, which can stabilize the polymer particles generated to form a stable latex. With particle sizes of ca. 1 to $15\text{ }\mu\text{m}$, dispersion polymerization can cover the particle size range between emulsion and suspension polymerization.

In aqueous *solution polymerization* a water-soluble monomer is polymerized to a water-soluble polymer. For example, polyacrylic acid is produced on a large scale by free radical techniques in this manner [10]. Again, the non-flammability and high heat capacity of water are advantageous. Such polymerizations in homogeneous solution can, in some cases, offer better molecular weight control by comparison to polymerization in a multiphase system.

7.1.2

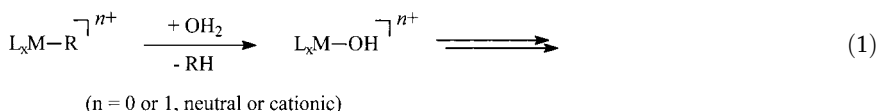
General Aspects of Transition Metal-Catalyzed Polymerization in Aqueous Systems

The previous section demonstrated the utility of polymerization reactions in aqueous systems. Carrying out transition metal-catalyzed polymerizations in aqueous systems is of great interest as they can afford a variety of new materials not accessible by established free radical techniques. Thus, various monomers subject to catalytic polymerization can not be polymerized by free radical polymerization, and catalytic polymerization also offers access to other polymer microstructures. In addition, control of free radical polymerization (e.g. with respect to molecular weight distributions) can be brought about by metal complexes.

Transition metal catalysis in aqueous media has developed into a broad field over the past two decades, and such reactions can by no means be regarded as exotic [11]. The Ruhrchemie-Rhone Poulenc process is applied commercially on a large scale. In this process, propene is hydroformylated using a rhodium catalyst in a biphasic aqueous system. Hereby, a simple separation of the water-soluble catalyst from the apolar products is enabled. To date, the majority of investigations have focused on the synthesis of low-molecular-weight compounds. However, as shown in the preceding section, polymerization reactions in aqueous systems are of particular interest [12]. A major reason why aqueous catalytic polymerizations had received relatively little attention for a long time is the notorious water sensitivity of the early transition metal-based Ziegler or Phillips catalysts [13–17] used for industrial olefin polymerization.

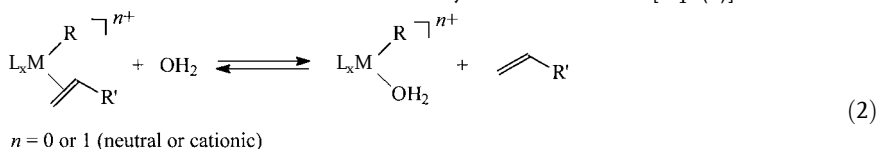
Although encapsulation techniques, e.g. in a hydrophobic polymer (*vide infra*), can restrict the access of water to the metal centers, a certain stability towards water of the different metal species involved in the polymerization reaction is desirable. Scheme 7.4 summarizes the mechanisms of various metal-catalyzed polymerizations.

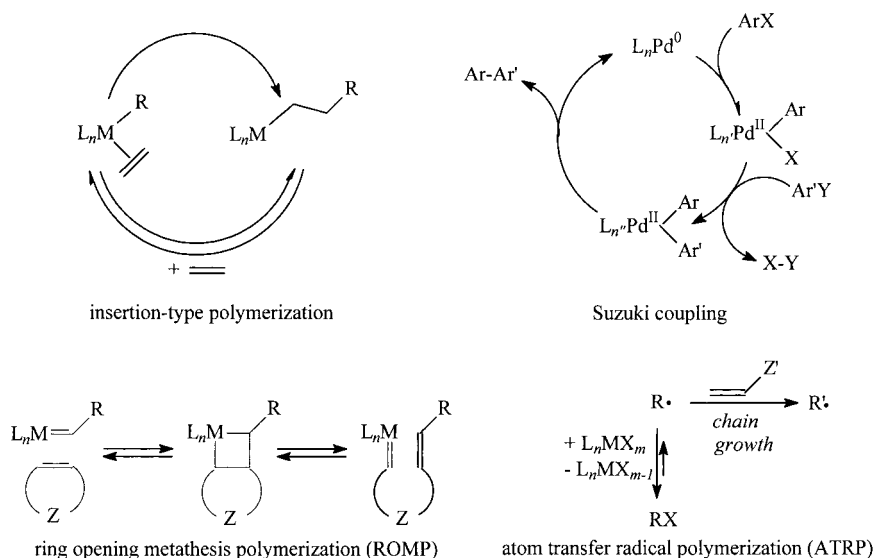
The majority of reactions involve organometallic species, most often metal-alkyl complexes. While such complexes are generally considered to be prone to hydrolysis [Eq. (1)], examples of quite stable alkyl complexes of late transition metals



(that is Group 8 to 10 metals) also exist (Section 7.2.2).

Also for species not involving metal-carbon bonds, such as in ATRP, possible hydrolysis of coordinating ligands (L) must be considered. Another reaction of general importance is the possibility of coordination of water as a ligand. Hereby, coordination sites can be blocked reversibly for the substrate [Eq. (2)].





Scheme 7.4 Schematic representation of the chain growth mechanisms of various metal-mediated polymerizations (R and Ar/Ar' =growing polymer chain. X = halogen).

Whereas early transition metal (that is metals of Group 4 to 6) centers generally strongly bind water, coordination to relatively less oxophilic late transition metal complexes can be comparably weak and does not pose a severe problem in many cases. Other possible side reactions are attack of water on coordinated olefin monomer or other ligands [18].

In addition to the reactivity of the catalytically active metal centers, a sensitivity of added co-catalysts towards water can obviously also be detrimental. For instance, Ziegler catalysts or metallocenes are most often employed with aluminum alkyls as co-catalysts. For polymerization in aqueous systems, catalysts which do not require water-sensitive co-catalysts are desirable.

This contribution reviews aqueous transition metal *catalyzed* polymerizations of olefinic monomers. Consequently, classical free-radical polymerizations employing metal-containing redox-systems as initiators, for example, are not considered.

To enable a comparison of polymerization of different monomers and of catalysts based on different metals, activities are usually given as turnovers per hour, $TO\ h^{-1}$ (TO =mol substrate converted per mol of metal). When comparing activities determined by different authors under strongly varying conditions the values should be taken as an indication of the order of magnitude. The same holds true for polymer molecular weights.

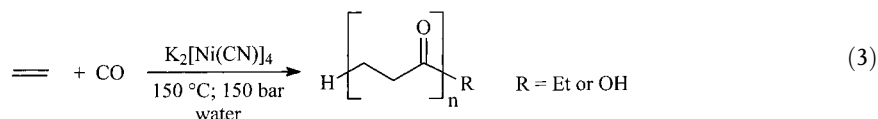
7.2

Catalytic Olefin and Alkyne Polymerization in Aqueous Systems

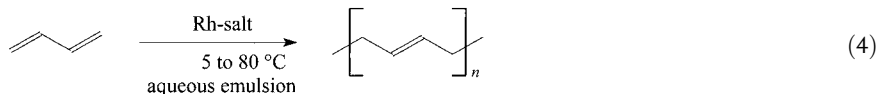
7.2.1

Historical Development

The reaction of ethylene with carbon monoxide in the presence of potassium tetracyanonickelate(II) can be regarded as the first example of an aqueous polymerization. In a patent filed 1948, Reppe and Magin described the formation of oligomers ($n=1, 2$) and higher “polyketones” [Eq. (3)] [19]. Albeit based on the analytical data provided it is unlikely that a true higher-molecular weight polymer was formed; without doubt several repeat units were incorporated per product molecule, a mechanistic feature which also applies to polymerization reactions.



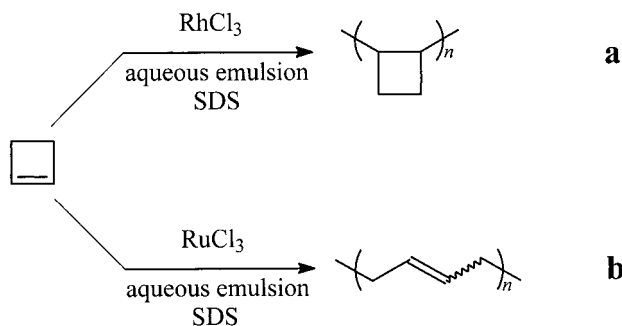
In the 1960s a number of publications on aqueous polymerizations of different monomers appeared. Rinehart et al. and Canale and co-workers independently reported aqueous polymerization of butadiene catalyzed by rhodium salts. Utilizing $\text{Rh}^{\text{III}}\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ as a catalyst precursor, semicrystalline *trans*-1,4-polybutadiene was obtained stereoselectively [Eq. (4); >99% *trans*] [20, 21].



By comparison, free-radical butadiene polymerization in aqueous emulsion typically yields polymers with 60% *trans*-incorporated units under similar conditions [22]. Polymer molecular weights of $2.6 \times 10^4 \text{ g mol}^{-1}$ were determined by light scattering [21].

A free-radical polymerization mechanism can be excluded on the basis of the polymer microstructure and experiments with radical inhibitors. Rhodium(I)-species, formed by reduction of Rh^{III} salts used as catalyst precursors by butadiene monomer, have been suggested as the active species. The catalyst is stable during the aqueous polymerization for over 30 h [23]. Catalyst activities are moderate with up to ca. $2 \times 10^3 \text{ TO h}^{-1}$ [24, 25]. By contrast to industrially important free-radical copolymerization, styrene is not incorporated in the rhodium-catalyzed butadiene polymerization [26]. Only scarce data is available regarding the stability and other properties of the polymer dispersions obtained. Precipitation of considerable portions of the polymer has been mentioned at high conversions in butadiene polymerization [23, 27].

Under similar conditions as those described by Rinehart for butadiene polymerization, Natta et al. investigated the polymerization of cyclobutene. With low conver-



Scheme 7.5 Aqueous cyclobutene polymerization by an insertion mechanism (a) and by ring opening polymerization (b); SDS= sodium dodecyl sulfate.

sions, they obtained a crystalline, highly stereoregular polymer (Scheme 7.5(a)) [28]. An insertion mechanism is evidenced by the intact ring structure of the polymer.

By contrast, in the presence of RuCl_3 as a catalyst precursor, ring opening polymerization of cyclobutene and 3-methylcyclobutene was observed exclusively (Scheme 7.5(b)) [29]. With low efficiencies of ca. 15 TO, low-molecular-weight stereoirregular oils were formed. Rinehart et al. have also reported ring opening polymerization of norbornene and of 2-functionalized norborn-5-enes with polar ester moieties in aqueous emulsion with moderate activities. Iridium(III) or Iridium(IV) salts in combination with a reducing agent, or Ir^{I} olefin complexes were employed as catalyst precursors. Norbornadiene and dicyclopentadiene were also polymerized, reacting with only one double bond [24, 30].

In summary, this pioneering work clearly demonstrated the possibility of aqueous catalytic insertion polymerization of acyclic and cyclic olefins, as well as aqueous ROMP. On the other hand, metal salts without any additional ligands to control the properties of the metal centers were utilized, and activation to the active species was probably also relatively ineffective in most cases. Consequently, catalyst efficiencies were moderate at best. Most of the polymerizations also afforded low molecular weight materials, or employed rather special monomers. The possibility of polymer latex synthesis appears not to have received much attention, although free-radical emulsion polymerization of styrene and butadiene was already a large-scale process at the time.

7.2.2

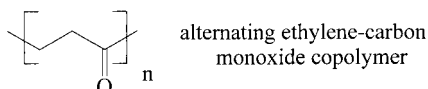
Recent Progresses in Catalytic Insertion Polymerization of Olefins

Since the aforementioned investigations, significant advances in aqueous catalytic insertion polymerization have only been made over the past decade. Alternating copolymerization of olefins with carbon monoxide, polymerization of ethylene and 1-olefins, and polymerizations of norbornenes and of butadiene have been studied.

7.2.2.1 Alternating Olefin/Carbon Monoxide Copolymerization

Since the aforementioned pioneering discovery of Reppe and Magin, catalytic olefin-CO copolymerization (in non-aqueous media) has found continuous, widespread interest. Carbon monoxide is an exceptionally cheap starting material, and the aliphatic alternating polyketones obtained possess attractive materials properties [31–33].

A major breakthrough has been the finding that catalysts based on cationic palladium(II) complexes with *bidentate* ligands, most often diphosphines, exhibit substantially increased activities in ethylene-carbon monoxide copolymerization by comparison to previously known nickel(II) and palladium(II) systems [34–38]. Methanol is typically used as a reaction medium, demonstrating the stability of these catalysts towards protic media.

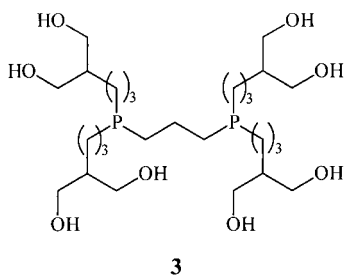
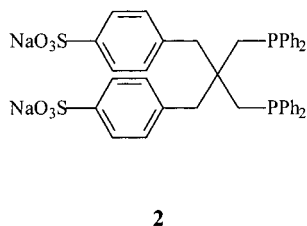
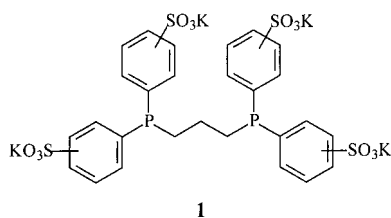


An alternating ethylene-CO copolymer melts at 257 °C. Incorporation of propylene decreases the melting point, enabling processing of the materials (e.g. 6 mol% propene: T_m 220 °C) [35]. Semicrystalline ethylene/propylene/carbon monoxide terpolymers have been commercialized by Shell as a new engineering thermoplastic termed CarilonTM since 1995, and BP has developed similar materials termed Ketonex [39, 40]. However, it has recently been announced that this business is to be abandoned for undisclosed reasons [41]. The polyketones have a good resistance to hydrocarbon solvents and good abrasion properties [42]. As a drawback, the presence of a large number of carbonyl groups renders the polymers sensitive to UV light, furthermore undesired condensation-crosslinking can occur at the high temperatures required for processing.

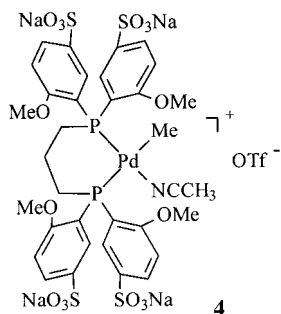
In 1994, Sen and Jiang reported aqueous ethylene/CO copolymerization by cationic palladium(II) catalysts with water-soluble bidentate sulfonated nitrogen- or phosphine-based ligands, such as **1**. At 50 °C and 35 bar each of ethylene and CO, moderate activities of up to ca. 10^2 TO h^{-1} were observed (with a catalyst prepared *in situ* from $[\text{Pd}^{\text{II}}(\text{NCCH}_3)_4](\text{BF}_4)_2$ /bidentate water-soluble ligand).

An alternating propylene-CO copolymer with a molecular weight of 1.4×10^4 g mol^{-1} (vs. polystyrene standards) was also prepared, albeit at lower rates [43]. A few years later, Sheldon et al. reported significantly higher activities of up to 1.5×10^4 TO h^{-1} in aqueous ethylene/CO copolymerization, using a very similar catalyst system comprising the same ligand **1**. These higher activities, comparable to those observed with 1,3-bis(diphenylphosphino)propane (dppp) as the non-sulfonated model for **1** in non-aqueous polymerization in methanol, were ascribed to a higher purity of the sulfonated phosphine ligand and the addition of a Brønsted acid, increasing catalyst stability. Molecular weights of the copolymer were found to be similar to materials obtained in methanol as a non-aqueous reaction medium under otherwise comparable conditions, with up to M_w 6×10^4 g mol^{-1} , M_w/M_n ca. 2.

A high catalyst stability in the aqueous reaction is evidenced by a constant productivity over several hours [44–46]. Specially designed water-soluble ligands with two sulfonated moieties attached to the C₃-ligand backbone (**2**) [47], or hydroxylated neutral ligands such as **3** [48] were found to display higher activities than **1**.



The introduction of methoxy substituents at the ortho position of the aryl rings of diphosphine-modified cationic palladium catalysts results in markedly increased catalyst performance [49]. With the fully *o*-OMe-substituted analogue of ligand **1**, ethylene-CO copolymers with molecular weights of up to M_w 1.2×10^5 g mol⁻¹ and narrow polydispersities (M_w/M_n ca. 2) were obtained in polymerizations in aqueous suspension. Employing the well-defined complex **4** of this ligand, under rather moderate conditions (90 °C, 30 bar each of ethylene and CO) high activities of 6.1×10^4 TO h⁻¹ have been reported [50].



As previously mentioned, the properties of olefin-CO copolymers depend strongly on the nature of the olefin employed. The glass transition temperature of 1-olefin-CO copolymers decreases from room temperature to nearly -60°C upon increasing the chain length of the 1-olefin from propylene to 1-dodecene [33]. By contrast to polar ethylene-CO copolymers, copolymers with higher 1-olefins display a hydrophobic character. For 1-olefin copolymerization, catalysts with entirely alkyl-substituted diphosphine ligands $\text{R}_2\text{P}-(\text{CH}_2)_n-\text{PR}_2$ ($\text{R}=\text{alkyl}$, by comparison to $\text{R}=\text{Ph}$ in dppp) such as **3** are particularly well-suited [48]. Ethylene-1-olefin-CO terpolymers and 1-olefin-CO copolymers can be prepared in aqueous polymerizations [43, 47, 48]. In the aforementioned copolymerization reactions, the polyketone was reported to precipitate during the reaction as a solid [45, 47, 48, 50]. However, in the presence of an emulsifier such as sodium dodecyl sulfate (SDS) and under otherwise suitable conditions, stable polymer latexes can be obtained. Such polymerizations can be carried out with water-soluble catalysts based on, e.g., ligands of type **3** [51]. By using a miniemulsion technique (*vide infra*) non-water-soluble catalysts can also be employed to prepare stable latexes [52]. Hereby, modification of the diphosphine ligands to attain water-solubility is not necessary, which can reduce synthetic effort. *In situ* catalyst systems $\{[\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2]\text{Pd}(\text{OAc})_2\}$ /strong acid ($\text{R}=\text{Ph}$ or $(\text{CH}_2)_{13}\text{CH}_3$) or well-defined complexes $\{[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]\text{PdMe}(\text{NCCH}_3)\}^+\text{Y}^-$ ($\text{Y}^-=[\text{B}\{3,5-(\text{F}_3\text{C})_2\text{C}_6\text{H}_3\}_4]^-$ or SbF_6^-) were used in the form of a solution of the palladium(II) complex in miniemulsion droplets of a hydrocarbon dispersed in the continuous aqueous phase (cf. Section 7.2.2.2 for the concept of catalyst miniemulsions). Catalyst activities of up to $5 \times 10^3 \text{ TO h}^{-1}$ slightly exceed those of non-aqueous polymerizations in methanol with the same catalysts, evidencing effective activation also of the *in situ* system despite the multiphase nature of the aqueous systems. Stable latexes of 1-olefin-carbon monoxide copolymers and of ethylene-undec-10-enoic acid-carbon monoxide terpolymers ($M_w > 10^4 \text{ g mol}^{-1}$ vs. PMMA standards) have been prepared (Fig. 7.1).

In the latter, the undecenoic acid termonomer, with a hydrophilic carboxylic acid moiety, can function as a copolymerizable stabilizer. By comparison to terpolymerization in non-aqueous polymerizations in methanol, the high local concentration of the liquid termonomer in droplets in the aqueous polymerization is beneficial for its incorporation. The 1-olefin copolymers exhibit glass transition temperatures of $T_g + 10$ to -55°C , and thus can form films upon drying of a latex at room temperature.

Regarding the mechanism of the aqueous polymerization, chain growth by alternating insertion of ethylene and CO in Pd-acyl or Pd-alkyl species, respectively, is identical to the well-investigated copolymerization in methanol. A significant difference is represented by hydrolysis as an important chain transfer step: in non-aqueous polymerization methanolysis of a Pd-alkyl species affords a Pd-OMe species which initiates chain growth, resulting in formation of a new $-\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OMe}$ endgroup in the polymer. By contrast, hydrolysis affords a Pd-OH species, which reacts with CO to form a Pd-hydride prior to initiation of the next chain (Scheme 7.6). Therefore, polyketones with two keto-endgroups are obtained preferentially or exclusively in the aqueous reaction [44, 47]. The

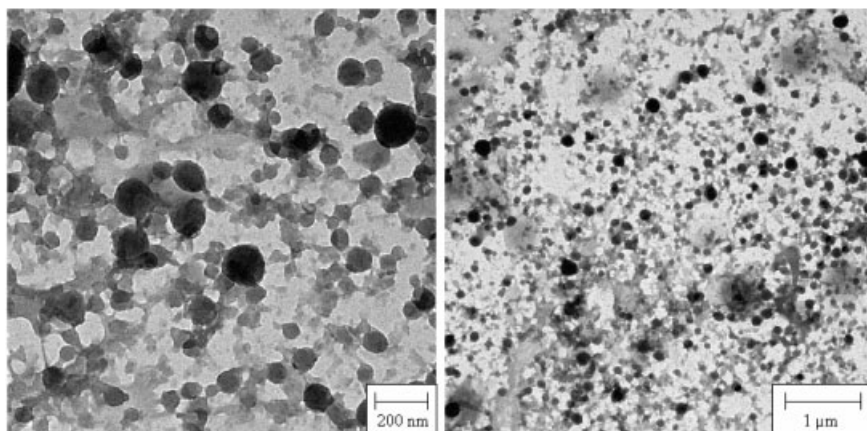
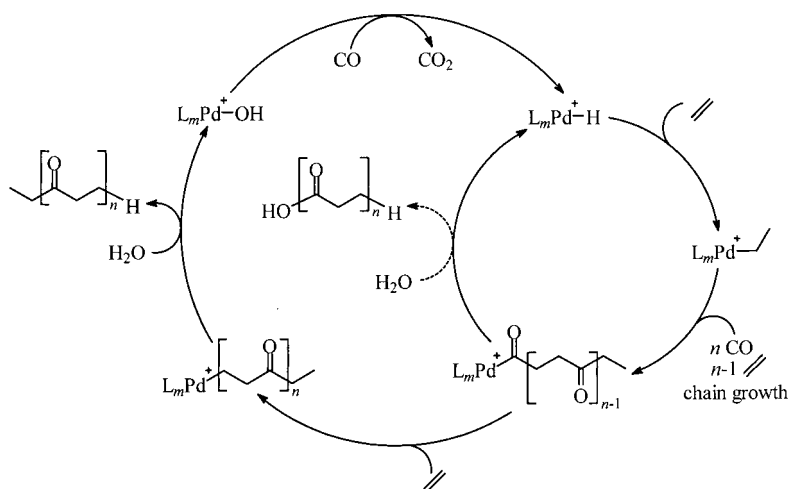


Fig. 7.1 TEM images of a polyketone latex [52].

aforementioned reaction can be regarded as a “reactivation” pathway after hydrolysis of a metal-alkyl bond, which is specific to aqueous reactions involving CO.



Scheme 7.6 Mechanism of aqueous ethylene-CO copolymerization [44, 47].

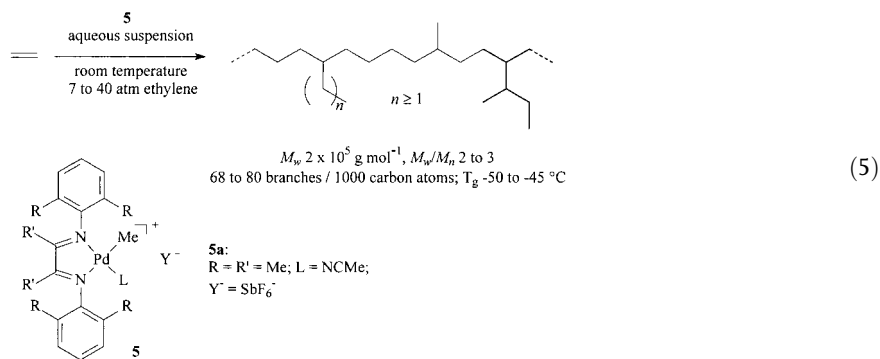
7.2.2.2 Polymerization of Ethylene and 1-Olefins

The discoveries of several new types of catalysts for (non-aqueous) ethylene and 1-olefin polymerization based on late transition metals over the last decade have initiated great interest in this field [16, 53–55]. By comparison to early transition metal-based Ziegler or Phillips catalysts used for industrial polyolefin synthesis [13–17], complexes of late transition metals are less oxophilic, and they can be much more stable towards polar media.

It can be noted that latexes of low-density polyethylene (LDPE) are prepared via free-radical emulsion polymerization as a specialty product [56]. However, the low variability with respect to the polymer microstructure is disadvantageous for tailoring latex properties (e.g. film-forming properties), resulting in a narrow property profile. In addition, working at pressures in excess of 1000 bar in the presence of water is challenging for the equipment used.

In 1993, Flood and co-workers reported ethylene polymerization in water using the rhodium complex $[(N-N-RhMe(OH_2)(OH))^+]$ as a catalyst precursor ($N-N-N=1,4,7$ -trimethyl-1,4,7-triazacyclononane) [57]. After 90 days of reaction at 60 bar ethylene pressure and room temperature, some low-molecular-weight polyethylene was obtained ($M_w 5 \times 10^3 \text{ g mol}^{-1}$). The amount of polymer obtained corresponded to 1 TO per day.

In 1995 Brookhart and co-workers reported that cationic diimine-substituted palladium complexes of type **5** [Eq. (5)] can polymerize ethylene to high molecular-weight, highly branched material in organic solvents such as methylene chloride.



The unique structure of the ethylene homopolymers obtained results from a propensity of the metal centers to “run” along the growing polymer chain between insertions (a similar behavior had been observed previously for 1-olefin polymerization by a neutral nickel catalyst by Fink et al.) [58, 59]. An extensive patent on these polymerizations was filed by Brookhart and DuPont, and McLain demonstrated in several examples that these polymerizations can also be carried out in water [60]. Detailed investigations by Mecking et al. revealed that in this suspension-type aqueous polymerization the catalyst is remarkably stable, ethylene being polymerized at a steady rate for several days [61, 65]. At slightly elevated ethylene pressures of 20 bar, with **5a** activities of 10^3 TO h^{-1} , similar to

non-aqueous polymerization in methylene chloride, are observed. However, this high stability is due to an “encapsulation” of the water-insoluble catalyst in the growing hydrophobic polymer, which protects the catalyst from access of water. Aqueous solutions of water-soluble derivatives of **5** with sulfonate-substituted diimine ligands are inactive for ethylene polymerization [62]. Mechanistic studies revealed that a complex of type **5** is stable in a water-containing solution, which means that neither the Pd-Me moiety nor the diimine ligand are hydrolyzed. However, decomposition occurred instantaneously upon addition of ethylene monomer [61].

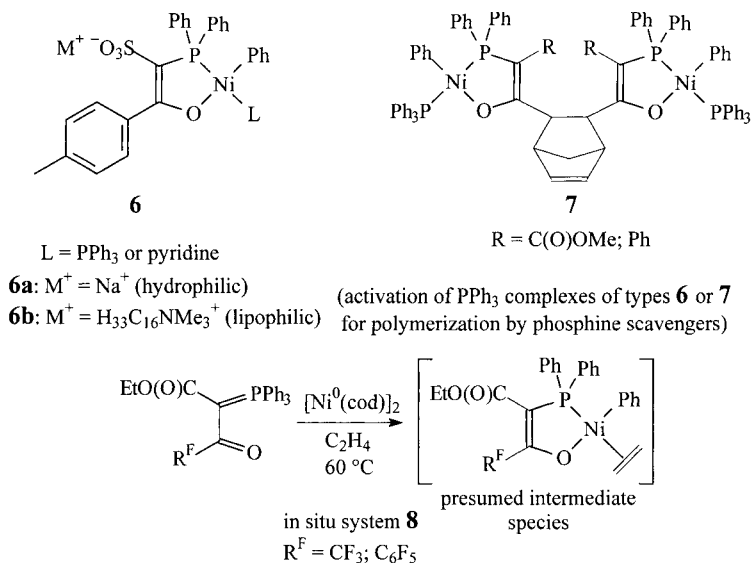
Regarding the possible undesired binding of water as a ligand [cf. Eq. (2)], in this cationic palladium system water coordinates weakly relative to ethylene, and does not block coordination sites for the monomer [63, 65].

Whereas traditional polymerization in methylene chloride under similar reaction conditions (temperature, ethylene pressure) affords a highly viscous liquid polyethylene (M_w 3×10^4 g mol⁻¹, ca. 100 branches/1000 carbon atoms, T_g -70°C), polymerization by **5a** in aqueous suspension yields a rubbery amorphous solid of significantly higher molecular weight and lower branching [Eq. (5)]. Rather than a conceivable direct interaction of water with the catalyst, this effect appears to be related to the different phases encountered by the catalyst during polymerization (heterogeneous aqueous suspension of polymer encapsulating the catalyst vs. homogeneous solution) [61]. Polymerization of 1-olefins by catalysts of type **5** in aqueous emulsion has been claimed to afford stable lattices [64].

In view of many potential applications, the synthesis of a largely linear polyethylene with some degree of crystallinity in aqueous emulsion would be of interest. Recently, Mecking et al. and Spitz et al. independently reported nickel(II)-catalyzed polymerization of ethylene to linear material in aqueous emulsion [65, 66]. Neutral nickel(II) complexes **6** and **7** (Scheme 7.7) based on known bidentate P-O-ligands [67–70] were found to be suitable catalyst precursors.

Using water-soluble catalyst precursors **6a**, stable latexes of low-molecular-weight polyethylene could be obtained [65, 71, 72]. For example, a dispersion of polyethylene of M_w 3×10^3 g mol⁻¹, M_w/M_n 2 to 3 was obtained with 10^3 TO h⁻¹ under moderate reaction conditions (70°C , 50 bar ethylene pressure). The catalysts are stable in the aqueous polymerization for several hours. With **7** significantly higher activities of up to ca. 3×10^4 TO h⁻¹ were observed in aqueous emulsion; however, the latexes prepared with these lipophilic catalyst precursors were reported to be colloiddally unstable [66, 73]. By comparison to traditional polymerization in non-aqueous organic media such as toluene, catalyst activities and polymer molecular weights are reduced in the aqueous polymerizations. The lower activities and molecular weights can be related to a lower rate of chain growth in the aqueous polymerization, caused by an insufficient local ethylene concentration at the catalytically active centers [71]. To improve catalyst performance, good catalyst activities at limited ethylene concentrations can be expected to be advantageous.

In this context, a systematic understanding of the relationship between catalyst structure and the effect of ethylene concentration on the chain growth rate is of interest. To date, however, there is no concise picture: for several neutral nickel



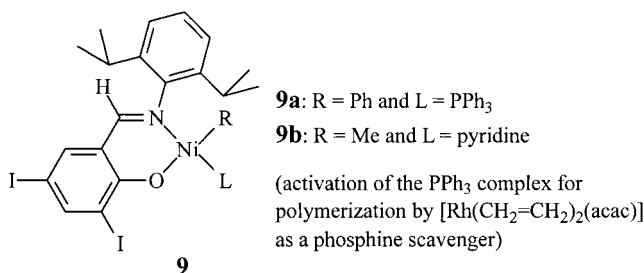
Scheme 7.7 Neutral nickel(II) complexes utilized for polymerization of ethylene in aqueous emulsion.

catalysts with bidentate ligands a strong dependence of chain growth rate on ethylene concentration has been reported (in organic solvents as a reaction medium) [74]. For very similar systems, though, a zero-order dependance on ethylene concentration has been found [75, 78]. Similarly, the polymerization of ethylene by cationic Pd^{II} or Ni^{II} diimine complexes investigated by Brookhart et al. is zero-order in ethylene [58], but very similar cationic catalysts with an osazone-moiety instead of the aryl-imine function were reported to be first order in ethylene [76]. It must be noted that in some aqueous polymerizations the local catalyst concentration (e.g. in a droplet) can be much higher than in traditional polymerizations in organic media.

By introducing electron-withdrawing perfluorinated substituents to the bidentate P–O-ligand (**8**; cf. Scheme 7.7), Claverie et al. have obtained highly active catalysts [77, 78]. At rates of up to $1.7 \times 10^5 \text{ TO h}^{-1}$ low-molecular-weight linear material ($M_w \ 3 \times 10^3 \text{ g mol}^{-1}$) can be obtained in aqueous emulsion at ethylene pressures of 25 bar. In contrast to the observations made with non-fluorinated ligands, these authors found no difference between the molecular weights of polymers obtained in aqueous and non-aqueous polymerizations. On the other hand, as for the non-fluorinated ligands, the activity is lowered in aqueous polymerization, hinting that, for these catalysts, chain growth and chain transfer have the same rate order dependence on ethylene concentration.

High-molecular-weight polyethylene has been prepared in aqueous polymerizations with a different class of catalysts [71, 82]. In traditional polymerization in toluene, suitable representatives of the aforementioned P–O-substituted catalysts and recently reported N–O-substituted salicylaldimine-based catalysts are known to af-

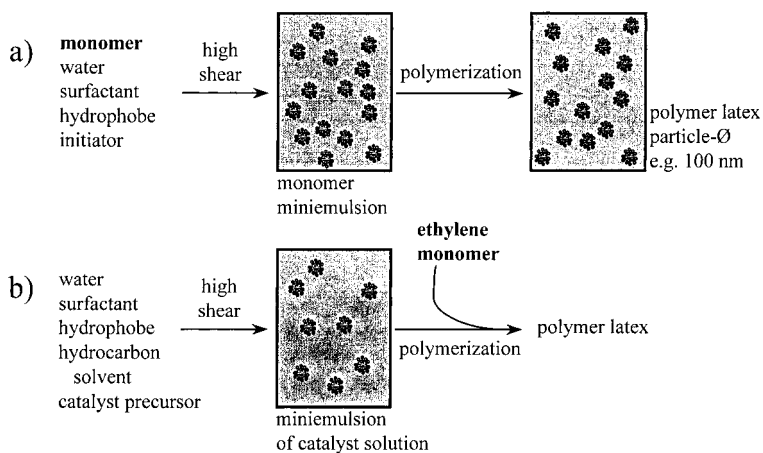
ford polymers of similar maximum M_w [68, 69, 79–81]. However, in contrast to the previously discussed aqueous polymerizations with P–O-substituted catalysts, the latter type of complexes was also found to yield high-molecular-weight material in aqueous polymerization. Semicrystalline polyethylenes of up to M_n 10^5 g mol $^{-1}$ with narrow polydispersities (M_w/M_n 2 to 4) are accessible in a suspension-type polymerization with precursors **9**.



Albeit these catalysts display a limited stability to water, activities of 3×10^3 TO h $^{-1}$ at room temperature are observed. As with the polymers obtained in traditional polymerization in organic solvents, the materials obtained in water with salicylalimine-based nickel(II) complexes possess a moderate number of methyl branches. Overall, as in the case of the linear polyethylenes obtained with **6** to **8**, the presence of water has no effect on the basic polymer microstructure. Polymer crystallinity can be influenced by employing norbornene as a co-monomer. High molecular weight, amorphous ethylene-norbornene copolymers, which form films at room temperature, can be obtained in aqueous polymerizations [71].

The synthesis of stable latexes requires suitable nucleation of primary particles and subsequent stabilization. In classical free-radical emulsion polymerization water-soluble initiators are used. Chain growth initially affords water-soluble oligomeric radicals, which can nucleate particles by collapsing upon themselves or by entering a surfactant micelle (cf. Section 7.1). Similar considerations appear reasonable for the aforementioned catalytic polymerization to stable latexes by the water-soluble complex **6a** (Scheme 7.7) [65, 71]. As a different strategy, a very fine initial dispersion of a *hydrophobic* catalyst precursor can be achieved as a solution in a large number of toluene/hexadecane miniemulsion droplets (\varnothing ca. 100 nm), dispersed in the continuous aqueous phase [77, 82].

As outlined in Section 7.1.1, miniemulsions are obtained by subjecting a mixture of water, a surfactant, an organic phase and a so-called hydrophobe to high shear. Miniemulsions can be stable over prolonged periods of time. Free-radical miniemulsion polymerization has been investigated extensively. It should be noted that the catalytic polymerization reactions of ethylene discussed in the following paragraph differ from typical free-radical polymerization of a preformed *miniemulsion of a liquid monomer* (Scheme 7.8). Gaseous ethylene monomer is fed continuously to the reaction mixture subsequent to *miniemulsification* of the catalyst solution. Thus, po-



Scheme 7.8 Typical free radical miniemulsion polymerization of a liquid monomer (a) vs. catalytic ethylene polymerization with a miniemulsion of a solution of the catalyst precursor (b).

lymerization of preformed miniemulsion droplets of monomer to particles of the same size, the typical feature of “miniemulsion polymerization”, does not apply.

The strategy of using a catalyst miniemulsion for latex synthesis offers two advantages: (a) catalyst precursors do not have to be modified hydrophilically, often reducing synthetic effort [77]; (b) somewhat water-sensitive precursors can be applied [82].

Employing miniemulsions of the aforementioned catalysts of type **8**, Claverie et al. have prepared stable latexes of low-molecular-weight linear polyethylene at high polymerization rates [77]. Latexes of ethylene copolymers with other olefins, such as undecene, tetradeca-1,13-diene or even styrene, have also been prepared [83]. Another significant advantage in such copolymerizations is that the high local concentration of the liquid co-monomer in droplets can enable high co-monomer incorporations, whereas in conventional ethylene copolymerizations, using late transition metal catalysts in organic media, incorporation of 1-olefins is usually low and requires addition of large amounts of the co-monomer. Copolymerization of ethylene with co-monomers bearing polar, hydrophilic moieties is of great interest in the context of polymer latexes. To date, ethylene copolymerization with undec-10-en-1-ol or ethyl undec-10-enoate has been reported [83]. By comparison to ethylene copolymerization with non-functionalized 1-olefins, no significant differences in polymerization rate are observed, indicating that there are no disadvantageous interactions between the polar moieties and the catalyst. As for the apolar olefins, co-monomer incorporation is high, due to the high local concentration of the liquid in droplets. A trade-off between the amount of incorporated co-monomer and polymerization activity is observed; an increased ethylene concentration under otherwise identical conditions results in higher polymerization rates but also lower incorporation. In all cases, the resulting copolymers were found to be very heterogeneous in nature,

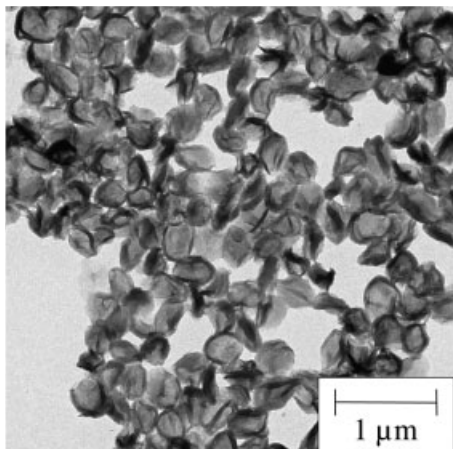


Fig. 7.2 TEM micrograph of polyethylene latex particles prepared by catalytic polymerization (M_w 2.1×10^5 g mol $^{-1}$, M_w/M_n 2.2; crystallinity 54%; catalyst precursor **9b**) [82].

due to significant co-monomer concentration drifts during the polymerization. This translates into T_m , as measured by DSC, spanning over as much as 60 °C.

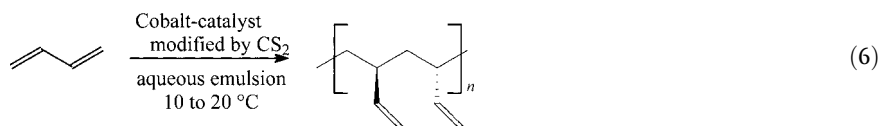
In the aforementioned ethylene polymerizations yielding stable latexes, low-molecular-weight polymer was obtained. To exploit the property profile of polymer latexes, the synthesis of dispersions of polyolefins with higher molecular weights is necessary. Mecking et al. have employed miniemulsions of the somewhat water-sensitive catalyst precursor **9b** for ethylene polymerization. Hereby, stable latexes of high molecular weight semicrystalline polyethylene (M_w 4×10^5 g mol $^{-1}$, M_w/M_n 2 to 4) could be obtained [82].

The polyethylene latexes obtained in the different emulsion polymerization procedures using the various aforementioned nickel(II) complexes display average particle diameters of 100 to 600 nm. A number of anionic surfactants or neutral stabilizers are suitable, i.e. compatible with the catalysts and capable of stabilizing the latex. Solids contents of up to 30% have been reported to date. A typical TEM image is shown in Fig. 7.2. By comparison to smooth, spherical latex particles of amorphous polystyrene as a well studied hydrocarbon polymer prepared by free-radical emulsion polymerization, the ruggedness of the particles shown can be rationalized by their high degree of crystallinity.

Very recently, an aqueous olefin polymerization using an early transition metal catalyst has also been reported [84]. A toluene solution of styrene is prepolymerized briefly by a catalyst prepared by combination of $[(C_5Me_5)Ti(OMe)_3]$ with a borate and an aluminum-alkyl as activators. The reaction mixture is then emulsified in water, where further polymerization occurs to form syndiotactic polystyrene stereoselectively. It is assumed that the catalyst is contained in emulsified droplets and is thus protected from water, with the formation of crystalline polymer enhancing this effect. Cationic or neutral surfactants were found to be suitable, whereas anionic surfactants deactivated the catalyst. The crystalline polystyrene formed was reported to precipitate from the reaction mixture as relatively large particles (500 μm).

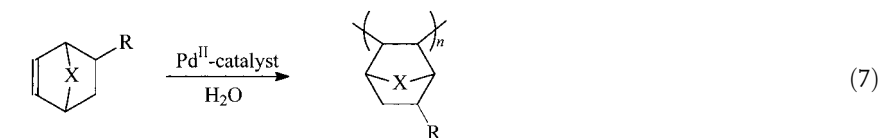
7.2.2.3 Miscellaneous Insertion Polymerizations

In addition to the previously mentioned rhodium-catalyzed butadiene polymerizations (Section 7.2.1), cobalt-catalyzed polymerization in aqueous emulsion has been investigated by workers at both Goodyear and a Japanese industrial group since the 1980s. In diene polymerization by late transition metal complexes, the growing polymer chain is generally assumed to coordinate to the metal center in a η^3 -allyl fashion [85]. In terms of the mechanism it is debatable whether chain growth by coupling of the polymer chain with coordinated monomer actually represents an insertion step or a concerted coupling reaction with formation of a new allyl moiety. Within the context of this section, it is reasonable, however, to discuss diene polymerization together with other insertion polymerizations. The *in situ* system $[\text{Co}^{\text{III}}(\text{acac})_3]/\text{AlEt}_3/\text{H}_2\text{O}/\text{CS}_2$ and other similar catalysts can yield highly crystalline syndiotactic 1,2-polybutadiene (T_m 205 °C) [86]. The high stereoselectivity of these catalysts has been ascribed to coordination of carbon disulfide to the metal center as a ligand [87]. Such stereospecific polymerizations can be carried out in aqueous emulsion [88–90], affording polymer latexes [Eq. (6)] [89].



A “prepolymerization” with a small portion of butadiene monomer in the presence of only trace amounts of water is required. A hydrocarbon solution of this “prepolymerized” catalyst mixture is subsequently dispersed in water, together with further butadiene, and polymerization proceeds. It has been speculated that the catalytically active species is shielded from water by the polymer formed during the “prepolymerization” [88].

Aqueous insertion-type polymerization of norbornene and substituted derivatives [Eq. (7)] has also been investigated. The tolerance of norbornene polymerization using $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$ as an initiator towards added amounts of water was noted by Risse and Mehler in 1992 [91].

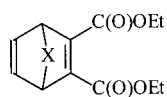


X = O; CH_2

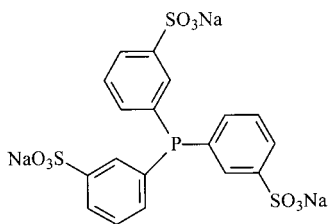
R = H, polar-functionalized substituent

In 1993, Perez et al. reported norbornene polymerization in aqueous emulsion at 70 °C using PdCl_2 as a catalyst precursor [92, 93]. A stable latex consisting of low-molecular-weight oligomeric material (degree of polymerization DP_n ca. 10) was obtained with low catalyst activities (70 TO h^{-1}). Very small latex particles of 10 to 20 nm diameter were reported. In the free radical polymerization of olefinic monomers such small particles are only obtained by microemulsion polymeriza-

tion. At the same time, Novak and Safir briefly reported polymerization of polar substituted norbornadienes **10** in aqueous emulsion with PdCl_2 [94].



(X = O; CH_2) **10**



TPPTS

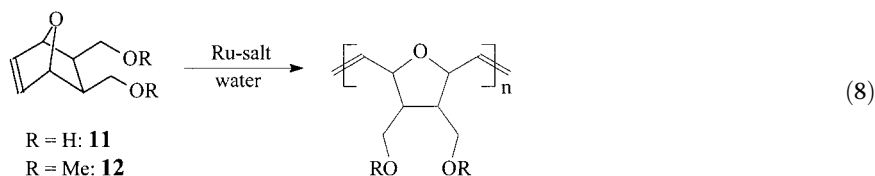
Rico-Lattes and co-workers have polymerized water-soluble norbornenes substituted with a gluconamide or a lactobionamide moiety with water-soluble $[\text{PdCl}_2(\text{TPPTS})_2]$ in aqueous solution [95]. Oligomers ($\text{DP}=17$ respectively 12) were obtained with moderate efficiency (ca. 10^2 TO over 24 h reaction time). Like their ROMP analogs, such glycopolymers have been suggested as therapeutic agents. Cell transfection by DNA complexes of a polyelectrolyte prepared by polymerization of an ionically-substituted norbornene has been investigated [96]. Goodall and co-workers have described the polymerization of butylnorbornene in aqueous suspension by the catalyst system $[\{(\text{allyl})\text{Pd}(\mu\text{-Cl})\}_2]/\text{TPPTS}/\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$, containing one equivalent of the water-soluble phosphine ligand TPPTS. A high activity of 4.5×10^4 TO h^{-1} has been reported in a patent, which considerably exceeds the moderate activities reported for the other palladium-catalyzed aqueous norbornene polymerizations [97]. This may be taken as an indication that significantly higher productivities can be achieved in vinylic polymerization of norbornenes in aqueous systems, compared to the moderate catalyst efficiencies reported to date.

7.2.3

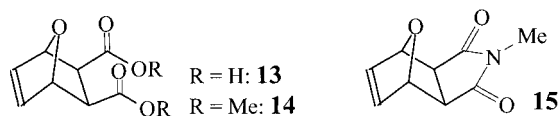
Recent Progresses in Ring Opening Metathesis Polymerization

Ring opening metathesis polymerization (ROMP; cf. Scheme 7.4) of cyclic olefins in non-aqueous media is applied commercially for the synthesis of a number of specialty polymers [98]. Poly(norbornene) is used as a synthetic rubber (Norsorex, Zeon Corp.). Amorphous polymers prepared by polymerization of norbornene derivatives (such as dicyclopentadiene) and subsequent hydrogenation of double bonds in the polymer are marketed for optical applications (Zeonex, Zeon Corp.). Poly(cyclooctene) is applied as a blend component in rubbers (Vestenamer, Degussa AG). Catalysts based on molybdenum, tungsten and ruthenium are most often used for ROMP [99, 100]. After first investigations in the 1960s (Section 7.2.1), a publication by Grubbs and Novak in 1988 attracted interest in aqueous ROMP [101]. Polymerization of functionalized 7-oxanorbornenes **11** and **12** in aqueous so-

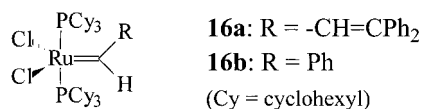
lution using RuCl_3 or $[\text{Ru}^{\text{II}}(\text{OH}_2)_6](\text{OTs})_2$ as catalyst precursors afforded high-molecular-weight polymer with narrow molecular weight distributions [$M_w = 1.3 \times 10^6$ g mol^{-1} ; M_w/M_n 1.2 for poly-**12**; Eq. (8)].



The aqueous solution of the catalyst can be recycled several times, which demonstrates a high stability towards water. The microstructure of poly-**12** prepared by aqueous ROMP with RuCl_3 or OsCl_3 was analyzed by Feast and Harrison. The polymers are atactic with a varying ratio of *cis*- vs. *trans*-double bonds in the backbone [102, 103]. A number of other functionalized norbornenes (**13** to **15**) have been polymerized to high molecular weight polymer in aqueous media [104–107]. As far as can be told from the published data, in all these cases the catalyst precursor and the monomer (**11**–**15**) initially formed a homogeneous solution, and the water-insoluble polymer precipitated during the polymerization reaction. Molecular weights can be regulated by adding acyclic olefins as chain-transfer agents [102, 104, 108].



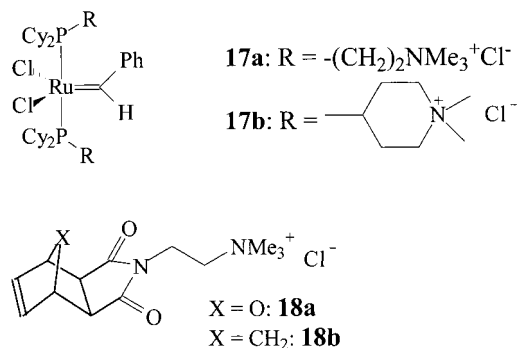
In the 1980s, well-defined metal alkylidenes were introduced as catalyst precursors for olefin metathesis [99, 109–111]. Especially for aqueous ROMP, ruthenium alkylidenes represent readily activated, well-defined, easy to handle catalyst precursors respectively initiators (for a living ROMP without chain-transfer, the term initiator appears more appropriate). Whereas in initial work vinyl-substituted carbenes (cf. **16a**) were employed [112], more straightforward routes to aryl-substituted carbenes (**16b**) were soon developed [113]. Today, vinyl-substituted carbenes are also accessible in one-pot procedures [114], and **16a** and **16b** are both commercially available.



Owing to the water-insolubility of these metal carbenes, aqueous polymerizations represent heterogeneous multiphase mixtures. Nonetheless, ROMP of the

hydrophilic monomer **15** or of a hydrophobic norbornene in aqueous emulsion (catalyst precursor **16a** or **16b** added as methylene chloride solution) or suspension can be living. For example, at a monomer to catalyst ratio **15/16b**=100, poly-**15** (78% yield) with M_w/M_n 1.07 vs. polystyrene standards was obtained [115]. As a surfactant for polymerization in emulsion, the cationic dodecyltrimethylammonium bromide (DTAB) was used preferentially. Block copolymers of narrow molecular weight distribution were also prepared.

With water-soluble carbene complexes **17** and water-soluble monomers **18**, living polymerization can be carried out in aqueous solution, without the addition of surfactants or organic cosolvents [116].



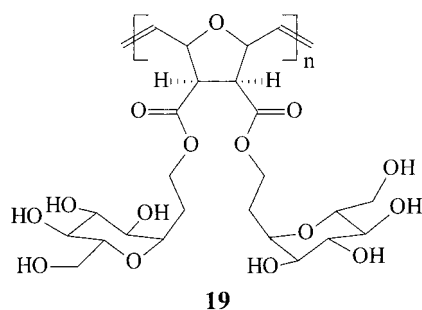
Addition of small amounts of acid (up to 1 equiv. DCl) is advantageous for catalyst performance. Remarkably the metal-alkylidene moiety is not attacked by the acid, but a monophosphine complex and the phosphonium salt of the ligand are formed instead. Monitoring of ruthenium-alkylidene species during the polymerization reaction by NMR confirms their high stability towards water.

ROMP of norbornene in aqueous emulsion employing ruthenium(IV) complexes [117] with bis(allyl) ligands such as the water-soluble $[(\eta^3\text{-C}_{10}\text{H}_{16})\text{Ru}(\text{OH}_2)(\text{OAc})]\text{BF}_4$ as catalyst precursors has been reported by Wache [118]. High molecular weight polymer with an unusually high *cis* content was obtained at rates of 100 TO h^{-1} .

Kiessling et al. have utilized ROMP for the synthesis of neoglycopolymers, i.e. for synthetic, non-natural polymers bearing carbohydrate moieties [119]. Carbohydrate-substituted monomers can be employed without protection of the hydroxo-groups, considerably reducing synthetic effort. As the monomers and also the desired polymers are water-soluble, aqueous ROMP can offer the advantage of a homogeneous reaction, which is beneficial for molecular weight control and catalyst efficiency.

The ROMP of 7-oxanorbornenes substituted with glucose or mannose moieties bound via C- or O-glycosidic linkages afforded neoglycopolymers, such as **19** [120, 121].

The polymerization can be carried out with an aqueous solution of RuCl_3 as a catalyst precursor. Relative molecular weights of ca. 10^6 by comparison to dextran



standards were estimated. The polymers contain *cis*- as well as *trans*-double bonds in the backbone in roughly equal amounts, which can be reduced to yield a saturated polymer by employing hydrazine reduction [121]. Utilization of alkylidene complexes **16** requires working in emulsion, owing to their water-insolubility (water/methylene chloride/surfactant) [122, 123]. In the ROMP of a carboximide-functionalized norbornene (cf. **15**) N-substituted with a carbohydrate moiety, increasing average degrees of polymerization in the range of $DP_n=10$ to 143 were observed with increasing monomer to catalyst ratio (**16b** as a catalyst precursor). This indicates a certain degree of molecular weight control, albeit molecular weight distributions were not reported [123]. The erythrocyte agglutinating activity of the protein concanavalin A can be inhibited by binding of carbohydrates. Structure-activity relationships have been investigated using carbohydrate-substituted polymers prepared by ROMP as multivalent inhibitors [120–122, 124].

In the aforementioned ROMPs in emulsion, the formation of a polymer latex has been noted briefly. Booth et al. reported the ROMP of the functionalized monomer **12** by $RuCl_3$ to give stable dispersions of high molecular weight polymer (10^5 g mol^{-1} vs. PS standards). A PEO-*b*-PPO-*b*-PEO copolymer was utilized as a steric stabilizer (PEO=poly(ethylene oxide), PPO=poly(propylene oxide)) [125]. Whereas the monomer is water soluble, the polymeric product is not, and in this respect the reaction resembles a dispersion polymerization. The stable latexes obtained consist of remarkably small particles of, e.g., 60 nm diameter. Emulsion polymerization of norbornene by various ruthenium catalysts has recently been investigated in detail by Claverie et al. [126]. Using the water-soluble carbene complex **17b** or the *in situ* system $[RuCl_2(TPPTS)_2]$ /ethyl diazoacetate as water-soluble catalysts, average activities of up to 10^4 TO h^{-1} were observed at 80°C in a 15 min polymerization experiment (for the structure of the water-soluble phosphine TPPTS cf. Section 7.2.2.3). Polynorbornene latexes consisting of relatively small particles of generally <150 nm diameter were obtained. The anionic surfactants SDS or Dowfax3B2 were used, and electrostatically stabilized latexes with solids contents of up to 46% were obtained with the latter surfactant (Dowfax3B2 is the disodium salt of disulfonated decyl-substituted diphenyl oxide). Unlike typical free radical emulsion polymerizations, the particle number increases continuously with conversion, indicating continuous nucleation. The observed dependence of particle numbers on reaction conditions indicates that homogeneous nucleation occurs, even in the presence of surfactant micelles. To

enable utilization of the commercially available hydrophobic carbene complex **16b** as a catalyst precursor for latex synthesis, the latter was employed as a solution in toluene/hexadecane miniemulsion droplets (cf. Section 7.2.2.2). Hereby, in addition to norbornene, cyclooctene and cyclooctadiene, which are unreactive towards the water-soluble catalysts, can be polymerized to latexes of high molecular weight polymers. Copolymerization of cyclopentene and cyclooctene by **16b** in miniemulsion has also been reported independently by Kühn et al. [127]. Copolymerization of norbornene with poly(ethylene oxide)-substituted norbornene macromonomers by **16b** to afford latex particles has been reported [128]. Although this reaction was carried out in ethanol/methylene chloride mixtures and thus does not represent an aqueous polymerization, from the viewpoint of colloid chemistry it is interesting that the concept of polymerizable stabilizers (“surfmers”) [129], well known from free radical polymerization, has been applied to a dispersion-type ROMP.

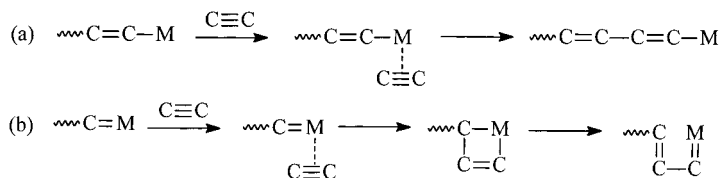
7.2.4

Recent Progresses in Catalytic Polymerization of Alkynes

7.2.4.1 Introduction

Twenty five years after the first report on catalytic polymerization of acetylene by Shirikawa, McDiarmid and Heeger [130], the Nobel prize has been awarded to these researchers for their contribution to the field of conducting polymers. Indeed, such polymers have promising applications such as low weight/high charge density batteries, polymer-modified electrodes, or capacitors to name only a few. Driven by these applications, different classes of polyacetylenes have been synthesized, starting from acetylene itself and from mono- or disubstituted acetylene derivatives.

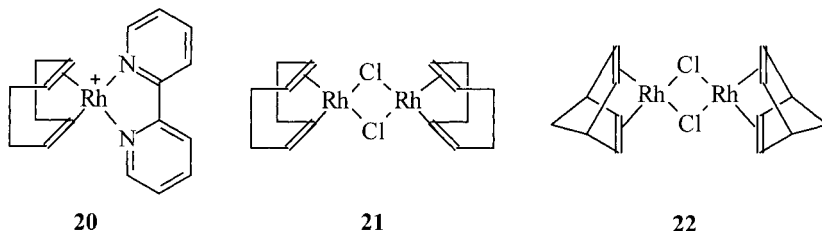
Alkyne polymerization in organic media has been reviewed [131]. A large variety of catalysts has been reported to polymerize alkynes in organic media. Similar to the polymerization of olefins, early transition metal as well as late transition metal catalysts are effective for this polymerization. Depending on the nature of the metal, two different mechanisms of polymerization have been suggested: polymerization via a metal alkyl intermediate, or via a metal carbene (Scheme 7.9). With metal alkyl complexes, polymerization proceeds via migratory insertion of the alkyne into the metal-carbon bond [path (a) in Scheme 7.9] whereas with metal carbenes the mechanism is equivalent to that of metathesis [path (b)].



Scheme 7.9 Mechanisms of alkyne polymerization.

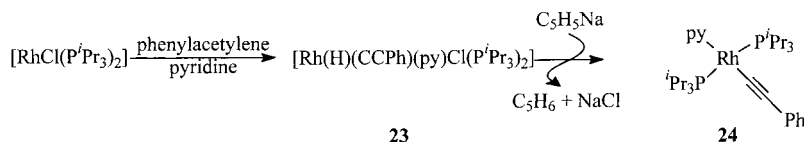
Most early transition metal complexes are considered to catalyze the polymerization through metal alkyl type intermediates. A typical example of such a catalyst, affording a high molecular weight polyacetylene [132], is $\text{Ti}(\text{O}^i\text{Bu})_4/\text{Et}_3\text{Al}$ [133]. The alkyl aluminum is thought to alkylate the titanium center, thus generating a titanium ethyl complex, in which migratory insertion occurs. As in 1-olefin polymerization, chain transfer proceeds via β -hydride elimination, generating a titanium hydride complex. Other catalytic systems include $[\text{V}(\text{mmh})_3]/\text{Et}_3\text{Al}$ [134], $[\text{Co}(\text{NO}_3)_2]/\text{NaBH}_4$ [135, 136] or $[\text{Fe}(\text{acac})_3]/\text{Et}_3\text{Al}$ [137] (mmh = 2-methylbutane-2,3-dionato; acac = acetylacetonate). The necessity of activating most of these complexes with aluminum alkyl co-catalysts is disadvantageous with regard to polymerizations in aqueous systems.

Although several rhodium carbenes (used in cyclopropanation of alkenes) are known, alkyne polymerization catalysts based on rhodium are thought to propagate in a similar fashion as early transition metal catalysts. To our knowledge, the first rhodium-based catalyst system was $\text{RhCl}_3/\text{LiBH}_4$ [138]. Subsequently, rhodium complexes **20** [139], **21** [139] and **22** [140] bearing diene ligands were then used for the synthesis of stereoregular *cis-transoidal* polyphenylacetylene with high polymer yield.



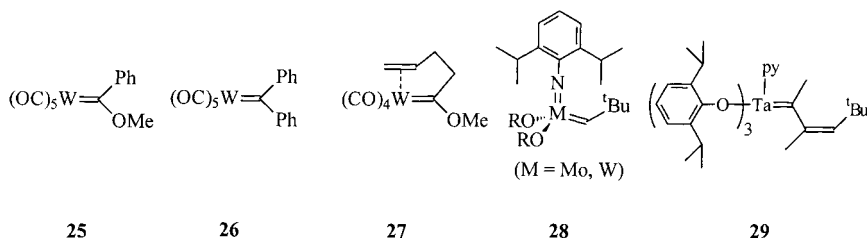
Usually, initiation of chain growth with rhodium catalysts does not require an alkylating agent. Kern has postulated the formation of an active species via oxidative addition of the terminal alkyne to rhodium, so-called hydroethynylation [138]. This reaction has also been reported by Werner et al. [141]: when contacting $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]$ with phenylacetylene in the presence of pyridine, the alkyne hydride complex **23** is generated (Scheme 7.10). In the presence of a base such as cyclopentadienyl sodium, a tetracoordinated Rh^{I} complex **24** was obtained and isolated.

Metals of Groups 5 and 6 (Nb, Ta, Mo and W) are known to form carbene complexes and are widely used in olefin metathesis [99, 100, 111]. Therefore, the polymerization of substituted alkynes with catalysts based on these metals is assumed



Scheme 7.10 Oxidative addition of phenylacetylene (py = pyridine).

to proceed via a metathesis-type mechanism. For catalysts prepared *in situ*, metal chlorides and metal carbonyls are the two most important classes of precursors. Alkyne polymerizations with metal chlorides (MoCl_5 , WCl_6 , NbCl_5 and TaCl_5) have been investigated by Masuda et al. [131]. MoCl_5 , without any additional co-catalyst, has been used for the synthesis of polyphenylacetylene [142] but the catalyst efficiency is greatly increased upon addition of a co-catalyst (such as $^n\text{Bu}_4\text{Sn}$, Et_3SiH , Ph_3Sb or Ph_3Bi) [143]. In addition to these ill-defined catalyst systems, alkylidene complexes based on tungsten (25–27 [144] and 28 [145]), molybdenum [145] (28) and tantalum [146] (29) have been synthesized and isolated prior to polymerization. These well-defined catalyst precursors do not require a co-catalyst for polymerization. Despite their advantages, these metals of Groups 5 and 6 are highly electrophilic, which is disadvantageous for their use in aqueous polymerizations.



7.2.4.2 Catalytic Polymerization of Alkynes in Aqueous Systems

As for other coordination polymerizations, the utilization of water as a reaction medium raises issues such as catalyst stability towards water, and miscibility of the monomers, polymers and the catalyst with water. Concerning the catalyst stability towards water, to date polymerizations of alkynes in aqueous systems have only been reported with rhodium and iridium catalysts. Unfortunately, the mechanism of polymerization with these complexes in non-aqueous, organic reaction media has not been completely elucidated (*vide supra*).

Blum, Schumann and co-workers reported the first study on alkyne polymerization with water-soluble rhodium complexes in homogeneous or biphasic aqueous systems [147]. Several complexes were utilized: $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{RhCl}(\text{tppms})_3] \cdot 4\text{H}_2\text{O}$ ($\text{tppms} = 3\text{-Ph}_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}$), $[\text{RhCl}(\text{cod})(\text{tppms})] \cdot \text{H}_2\text{O}$ ($\text{cod} = 1,5\text{-cyclooctadiene}$), $[\text{Rh}(\mu\text{-}3\text{-Ph}_2\text{PC}_6\text{H}_4\text{SO}_3)(\text{cod})]_2$, $[\text{Rh}(\mu\text{-SPh})(3\text{-Ph}_2\text{PC}_6\text{H}_4\text{CO}_2\text{H})(\text{CO})]_2$ and the cluster $[\text{Rh}_3\text{O}(\text{OAc})_6 \cdot (\text{H}_2\text{O})_3]\text{OAc}$. Trimerization of propynoic acid and oligomerization of phenylacetylene were investigated with these catalyst precursors.

In the cyclotrimerization of propynoic acid, trimellitic ($1,2,4\text{-C}_6\text{H}_3(\text{CO}_2\text{H})_3$) and trimesic acid ($1,3,5\text{-C}_6\text{H}_3(\text{CO}_2\text{H})_3$) are obtained as the product of head-to-head or head-to-tail linkage, respectively. For the sake of comparison, reactions were conducted both in neat water and in neat THF. In all cases, the yield of the trimer was higher in the aqueous system, evidencing the high tolerance of the rhodium catalyst towards water.

Polymerization of the water-insoluble monomer phenylacetylene with the same catalysts was investigated in both homogeneous (THF) and biphasic systems (toluene/water 5:1). In the biphasic mixture, $[\text{RhCl}(\text{cod})(\text{tppms})] \cdot \text{H}_2\text{O}$ afforded a polymer with a low activity (ca. 10 h^{-1}), whereas all other catalysts only dimerized or trimerized the monomer. By comparison, in refluxing THF solution, $[\text{RhCl}(\text{cod})(\text{tppms})] \cdot \text{H}_2\text{O}$ yielded only low oligomers with a very low activity ($\text{TO} = 1.5 \text{ h}^{-1}$). The reasons for this apparent enhancement in propagation rate in the presence of water are unclear.

Subsequently, Tang et al. studied the polymerization of phenylacetylene and of para-substituted phenylacetylenes with lipophilic and water-soluble catalysts [148]. With $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (**22**; nbd = norbornadiene), a strong influence of the nature of the solvent on the polyphenylacetylene yield was observed. Whereas almost no polymer is obtained in toluene, 58% conversion is observed in water within 30 min (corresponding to 264 turnovers). This effect is even enhanced with (*p*-methylphenyl)acetylene as a monomer. The polymer molecular weight also increased on going from toluene to water, the polyphenylacetylene obtained in the aqueous system being insoluble even in THF. These two effects are intriguing as neither the catalyst nor the monomer have been noted to be soluble in the reaction medium. Similar results in terms of polymer yield and of molecular weight were obtained with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (**21**) in water. The polymer microstructure is highly stereoregular with a *cis* content of 94% as determined by the method of Simionescu and Percec [149]. Unfortunately, polymerization in pure phenylacetylene monomer has not been reported and therefore it is not possible to conclude whether water is only a dispersion medium or if it interacts with the catalyst.

Aqueous polymerizations of phenylacetylene have been carried out with several other rhodium complexes of the general formula $[\text{RhCl}(\text{cod})(\text{L})]$, L representing a nitrogen-based ligand, such as NH_3 , $t\text{BuNH}_2$, piperidine or *N*-methylimidazole [148]. These catalysts also afford high polymer yields, with polymer molecular weights between 7×10^3 and $2.3 \times 10^4 \text{ g mol}^{-1}$ (M_w/M_n around 2) with a high *cis* content (around 85%).

Besides this work with rather lipophilic catalyst precursors, two water-soluble analogues have been investigated: $[\text{Rh}(\text{tos})(\text{cod})(\text{H}_2\text{O})]$ (**30**; tos = tosylate) and the similar compound $[\text{Rh}(\text{tos})(\text{nbd})(\text{H}_2\text{O})]$ (**31**) [148]. The authors have verified that water is still the best reaction medium for polymerization of phenylacetylene compared to toluene, THF and neat monomer, thus indicating a possible involvement of water in the formation of the active catalyst (830 TO in water). With catalyst precursor **30**, low polydispersities and a *cis* content of 90% are found, whereas catalyst precursor **31** affords a larger polydispersity but a higher *cis* content (100%). Interestingly, these catalysts proved to be tolerant to air since similar polymerization results are obtained with tap water without exclusion of air.

Joo et al. utilized the highly water-soluble rhodium complex $[\text{RhCl}(\text{CO})(\text{TPPTS})_2]$ for the polymerization of terminal alkynes (phenylacetylene and (4-methylphenyl)acetylene; for the structure of TPPTS cf. Section 7.2.2.3) [150]. This catalyst selectively produces *cis*-transoid polymers at room temperature in homogeneous solution in water/methanol mixtures, as well as in biphasic mixtures of water and chloro-

form. The rate of polymerization is higher in the homogeneous medium ($\text{H}_2\text{O}/\text{MeOH}$) than in the biphasic one ($\text{H}_2\text{O}/\text{CHCl}_3$). The iridium analog of this complex, $[\text{IrCl}(\text{CO})(\text{TPPTS})_2]$, shows catalytic activity for the polymerization of phenylacetylene only at elevated temperature, to give *trans*-polymers. The polymerization rate increases significantly when trimethylamine N-oxide (Me_3NO) is added to the reaction medium. The function of this reagent is unclear but it is considered to be a weakly coordinating ligand and could act as a stabilizing agent in the reaction.

The few aforementioned examples of alkyne polymerization in aqueous systems are restricted to phenylacetylene and its *p*-methyl derivative. It has even been reported that polymerizations of aliphatic acetylenes such as $\text{HC}\equiv\text{CR}$ ($\text{R}=\text{C}_6\text{H}_{13}$, $(\text{CH}_2)_2\text{OH}$, $(\text{CH}_2)_3\text{CO}_2\text{H}$) and $\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$ failed with the water-soluble precursor **30** [148]. However, Yashima and co-workers have recently reported successful polymerization of the acid functionalized alkynes (4-carboxyphenyl)acetylene [151] and propynoic acid [152] in water. Poly(4-carboxyphenyl)acetylene had previously been prepared via a three step procedure: protection of the acid as the ethyl ester, polymerization in THF with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (**22**), and subsequent polymer-analogous hydrolysis of the ester moieties [153]. By contrast, aqueous polymerization in the presence of a base advantageously allows for the direct synthesis of poly(4-carboxyphenyl)acetylene [152]. Deprotonation is necessary as acids can be detrimental for polymerization – acetic acid is used as a termination reagent to cleave the metal from the polymer [154]. This polymerization was carried out with various complexes ($[\text{Rh}(\text{cod})_2]\text{BF}_4$ **32**, $[\text{Rh}(\text{nbd})_2]\text{ClO}_4$ **33** and $[\text{Rh}(\text{tos})(\text{cod})(\text{H}_2\text{O})]$ **30**), which are reported to be water soluble. Polymers with molecular weights between 2.9×10^4 and $1.6\times 10^5 \text{ g mol}^{-1}$ ($M_w/M_n > 2$) with a *cis-transoidal* highly stereoregular structure were obtained in good yields. Polymerization of propynoic acid was also investigated with the same catalyst precursors, **30**, **32** and **33**, in presence of a base to deprotonate the monomer [152]. By comparison to polymerization of (4-carboxyphenyl)acetylene (66 TO h^{-1}), the reaction is slower (5 TO h^{-1}). The polymer microstructure is highly *cis-transoidal* (but isomerization from *cis* to *trans* configuration is observed upon converting the sodium carboxylate form of the polymer into the carboxylic acid).

7.2.5

Summary

Investigations in the 1960s clearly demonstrated the possibility of catalytic olefin polymerization in aqueous systems. Albeit various types of monomers were polymerized via different polymerization types, in most cases rather special monomers were employed or products of low molecular weight were obtained. The utilization of ill-defined catalyst precursors often resulted in low catalyst efficiencies; in addition, the possibility of polymer latex formation was given little attention. Since then, considerable advances have been achieved only during the past decade. The scope of polymers prepared in aqueous catalytic polymerizations has grown substantially, catalyst activities have been increased by two orders of magnitude already, and the preparation of stable aqueous polymer latexes has been studied. Olefin-CO copolymeriza-

tion in *aqueous* systems can afford high-molecular-weight aliphatic alternating polyketones at rates similar to the commercial process performed in methanol as a non-aqueous medium (up to 6×10^4 TO h^{-1}). Stable latexes can also be prepared. By proper choice of the olefin component(s), the glass transition temperature can be adjusted to values desirable for film formation under ambient conditions. The accessibility of latexes may enable new applications, which also do not require processing of the polyketones at disadvantageously high temperatures. Ethylene polymerization in aqueous systems can be carried out with a variety of different catalysts, affording high-molecular-weight completely amorphous or semicrystalline polymer. In particular, stable latexes of largely linear polyethylenes have been prepared. Copolymerization with various olefinic monomers enables a control of polymer crystallinity. High catalyst activities have already been achieved in the synthesis of latexes of low-molecular-weight material (up to 2×10^5 TO h^{-1}). Such polymerizations can be of interest as a convenient direct route to wax-dispersions. The accessibility of latexes of high-molecular-weight polyethylene has also been demonstrated (M_w 4×10^5 g mol^{-1} ; M_w/M_n 2 to 4). In olefin polymerization as well as CO copolymerization, a limited conversion of liquid 1-olefin (co)monomers is yet to be overcome in many cases. As an example of properties that could find potential application, polyolefins contain a negligible proportion of double bonds by comparison to styrene-butadiene copolymers, a hydrocarbon polymer currently prepared by free-radical emulsion polymerization on a large scale. This can result in a considerably higher stability towards UV-light and air of polymer films formed from polyolefin latexes.

ROMP in aqueous systems has been investigated intensively. A broad range of monomers, including many water-soluble norbornene derivatives, can be polymerized to high-molecular-weight hydrophilic or lipophilic materials. Utilization of well-defined metal carbenes as catalyst precursors respectively initiators enables molecular weight control and living polymerization, and water-soluble ruthenium carbenes have recently become available. Whereas, typically, monomer/metal ratios of 100:1 have been applied in reactions of polar-substituted norbornenes, activities of up to 10^4 TO h^{-1} have been observed to date in the synthesis of polynorbornene latexes. Aqueous ROMP represents a versatile synthetic route to specialty materials, e.g. resultant water-soluble polymers have been used for biomedical investigations. Aqueous polymerization of *butadiene* and *norbornenes*, as well as *alkynes* has also been studied, and stable latexes can also be obtained in various cases.

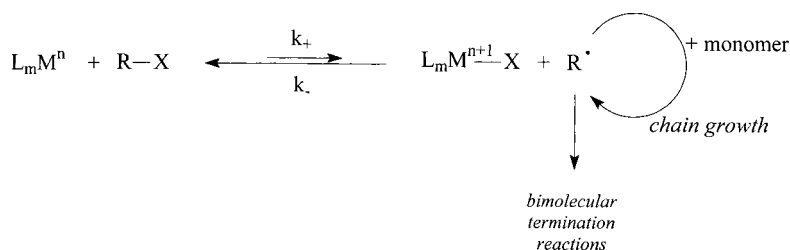
7.3

Controlled Free-Radical Polymerization in Aqueous Systems with Metal Complexes

7.3.1

General Features of Atom Transfer Radical Polymerization (ATRP)

Radical polymerizations can be controlled by addition of a suitable metal complex, which reversibly transforms the free radicals into a dormant species. Such is the case in atom transfer radical polymerization (ATRP) [155, 156]. Contrary to the



Scheme 7.11 Mechanism of atom transfer radical polymerization (ATRP).

polymerizations discussed in the previous section, polymerization does not proceed via active species with a metal-carbon bond (Scheme 7.11): in ATRP, the metal complex promotes atom transfer, and an alkyl halide is used as an initiator.

At the very beginning of the polymerization, the reaction of the halogenated initiator and the metal species generates a metal halide complex and radicals in high concentration, yielding polymers with polydispersities and molecular weights characteristic of an uncontrolled polymerization. Because the radical concentration is high, termination via radical-radical coupling or disproportionation are frequent events. However, the metal halide complex is specifically designed to react with free radicals and to act as a spin trap. The kinetics of the metal promoted radical trapping reaction are known to be very fast, e.g. $k_- = 1.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ at 110°C for styrene polymerization catalyzed by $[\text{CuBr}_2(\text{dNbpy})]$ (structure of dNbpy cf. page 262) [157].

Soon, due to radical termination, an excess of metal halide is present and radicals are more likely to react back to the dormant form than to terminate (persistent radical effect) [158, 159]. Under these conditions, a metal-catalyzed equilibrium between dormant and active chains is established and the reaction is controlled: the average molecular weight grows linearly with conversion and the polydispersity remains close to 1. The tradeoff in return for achieving polymer molecular weight control is a slow polymerization rate, which is characteristic for ATRP.

The kinetics are dependent on the nature of the metal complex and also on the relative amount of initiator. Usually, the organic halide used as an initiator and the metal compound are employed in a 1:1 molar ratio as control of molecular weight is optimal under these conditions, but higher ratios can also be used [155]. The metal compound is thus effective in “catalytic amounts”. It should be noted that by contrast to, for instance, olefin polymerization the metal complexes involved in ATRP are not directly part of the polymerization chain growth cycle. Nonetheless, they are usually designated as catalysts in the literature, and this designation is adopted throughout this section.

Although many different catalytic systems, based on Fe^{II} [160–163], Ni^{II} [164–66], Re^{V} [167], Mo^{V} [168], Mo^{III} [169], Pd^0 [170], Co^{II} [171], and Rh^{I} [172, 173], exist the most extensively investigated systems are Cu^{I} based [174–182] – first devel-

oped by Matyjaszewski [183–193] – and Ru^{II} systems, developed by Sawamoto [194–197].

The ATRP mechanism does not involve any metal-carbon bond potentially sensitive towards water. Free radicals, representing the actual active species, are also known to be stable in water. However, ATRP in aqueous media often results in loss of polymer molecular weight control. This is due to the very high intrinsic reactivity of most water-soluble monomers, and for ionic monomers the formation of highly viscous polyelectrolytes. Regarding the stability of the transition metal complexes involved, reversible dissociation into cations and halogen anions can occur in water, but this does not affect the control of polymerization. Hydrolysis of Schiff base ligands [178] or displacement from the metal center by water as a ligand [156] can occur occasionally.

7.3.2

Polymerization of Water-Soluble Monomers by ATRP

Control of the polymerization of water-soluble monomers by ATRP is of particular interest, as free-radical polymerization today is the only viable route for the synthesis of industrially relevant water-soluble polymers.

Numerous water-soluble monomers have been polymerized via ATRP (Fig. 7.3). Polymerization of acrylic and methacrylic monomers can be problematic as these monomers often contain trace impurities of acrylic or methacrylic acid (MAA). The presence of these carboxylic containing monomers can be detrimental: for example, Matyjaszewski et al. have observed that (non-aqueous) polymerization of acrylic acid cannot be controlled with $[(\text{bpy})_2\text{CuCl}]$ ($\text{bpy}=2,2'$ -bipyridine), as the monomer (and the polymer) is likely to coordinate to the metal center, to form a species that is unable to control the polymerization [198].

The very first example of aqueous controlled radical polymerization was reported by Matyjaszewski et al. with the polymerization of **34** (HEA), catalyzed by CuBr/bpy in water at 90°C [199]. Contrary to polymerizations carried out in or-

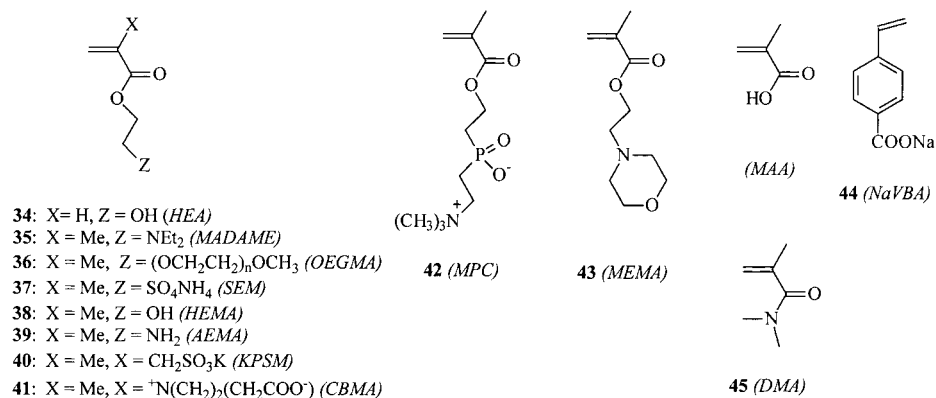
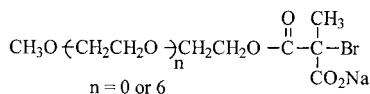
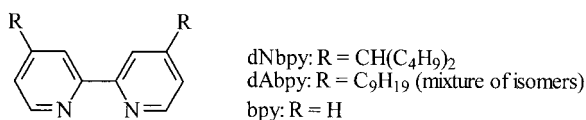


Fig. 7.3 Water-soluble monomers polymerized by ATRP (common acronyms given in brackets).

ganic solvents with this catalyst system, the catalyst is homogeneously dissolved in a 50:50 mixture of water and HEA-monomer. High conversions (87%) are achieved after 12 h, and the resulting polymer has $M_n = 1.47 \times 10^4 \text{ g mol}^{-1}$ and $M_w/M_n = 1.34$.

Armes et al. have intensively studied the aqueous ATRP of various monomers. Using CuBr/bpy as a catalyst, methacrylic acid polymerization has been shown to be possible in aqueous media at pH values between 6 and 9 [200]. The polymerization occurs very slowly (80% conversion after 21 h at 90 °C, [monomer]:[initiator]:[catalyst]=28:1:1) yielding polymers with low molecular weight ($M_n = 2.9 \times 10^3 \text{ g mol}^{-1}$) and a polydispersity of $M_w/M_n = 1.3$. This is probably due to a loss of catalytic species occurring from the competitive coordination of carboxylic acids to the copper centers, as mentioned for the case of acrylic acid. The choice of pH is important: at pH < 6, protonation of the bipyridyl ligand occurs, resulting in loss of control. The choice of initiator is equally important: the polymerization is only controlled when the methoxy-capped macroinitiator **46** is used.

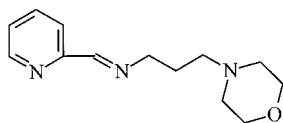


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Contrary to methacrylic acid, which is only polymerized slowly at 90 °C, **36** (OEG-MA) undergoes quantitative ATRP in 30 min at room temperature, using the system CuCl/bpy [201, 202]. Very high ATRP rates seem to be a general observation for a range of water-soluble monomers: indeed, quantitative and controlled polymerizations are observed for **44** (NaVBA) [203] (pH=11), **42** (MPC) [204] (pH=7), **43** (MEMA) [205] (pH=7), **41** (CBMA) (pH=7) [206], **37** (SEM) [207], **39** (AEMA) [207], and **35** (MADAME) [208, 209]. In all cases, CuBr/bpy or CuCl/bpy was used as a catalyst, in combination with a 1-ketobromo compound. The motivations underlying the choice of CuBr versus CuCl are not presented: a study by Matyjaszewski [210] et al., supported by a recent study by others [211], indicates that, as CuCl has a lower oxidation potential than CuBr, the rate of activation k_a is higher. (k_a , which together with k_t , determines the radical concentration, is usually close to diffusion limited.) Consequently, polymerization rates are expected to be faster with CuCl/bpy systems. Indeed, for methacrylic monomers, the CuCl/bpy system was used preferentially by Armes (with the exception of **42** (MPC) [204] and **38**

(HEMA) [212]). Monomer **42** (MPC) spontaneously polymerizes at room temperature in aqueous solution and the choice of the slowest catalyst is therefore justified. Because poly-**38** [212] is not soluble in water, the polymerization is run in a 50:50 MeOH:water mixture. Consequently, rates are lower than in water (95% conversion requires 3–4 h reaction time at room temperature). A comparison of polymerization rates in aqueous and non-aqueous media reveals strong solvent effects. Polar solvents have been found to increase the polymerization rate, possibly because of the combined effect of an increase of rate constant k_+ [213] and a competitive coordination of the solvent and the ligand in the copper species [214].

CuX/bpy (X=Cl, Br) is not the only catalyst efficient in aqueous ATRP. Pelton et al. have extensively studied the polymerization of **35** (MADAME) in organic solvents [209] and aqueous media [215] at room temperature, and found that CuBr/HMTETA (HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetraamine) is less effective in ensuring molecular weight control than CuBr/bpy under similar conditions. Using methyl bromophenylacetate as an initiator, the conversion in aqueous polymerization is similar with both catalyst systems CuX/bpy and CuBr/HMTETA (85% conversion at room temperature), affording, however, monodisperse polymers for the former ($M_n = 1.28 \times 10^4$ g mol⁻¹, corresponding to the theoretically calculated M_{nth} ; $M_w/M_n = 1.2$) and polymers with broader molecular weight distribution for the latter ($M_n = 1.84 \times 10^4$ g mol⁻¹; $M_w/M_n = 1.5$). Excellent control in the aqueous polymerization of **36** (OEGMA) can be achieved with a copper-based catalyst with ligand **47** [216]. Unexpectedly, the Schiff base ligand is not hydrolyzed during the polymerization reaction, and at room temperature a polymer of $M_n = 1.2 \times 10^4$ g mol⁻¹ ($M_w/M_n = 1.18$) is obtained in 93% yield after a reaction time of only 4 h.



47

Despite the large numbers of water-soluble monomers that can be polymerized by ATRP, several problems remain to be solved. For example, Brittain et al. [217] have shown that the aqueous polymerization of **45** (DMA), catalyzed by CuBr/L (L=HMTETA, tris[2-(dimethylamino)ethyl]amine (Me₆-TREN) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me₄Cyclam)) is not controlled because of the slow but irreversible decomposition of the bromo-terminated end-group of the dormant chains. Aqueous polymerization of acrylic [199] and styrenic monomers [203] also appears to be difficult to control, as implied by the rarity of known examples.

Except in the case of polymerization of **38** (HEMA), water-soluble polymers are formed in all the polymerizations regarded, and in this sense the reactions can be designated as solution polymerizations.

7.3.3

Polymerization of Water-Insoluble Monomers by ATRP

The first example of the ATRP of methyl methacrylate (MMA) in an aqueous system was reported in 1996 by Granel et al. [164]. Using $[\text{Ni}^{\text{II}}\text{Br}\{\kappa^3\text{-N,C,N-1,3-(CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3\}]]$ as a catalyst precursor and 2-ethylbromoisobutyrate as an initiator, suspension polymerization of MMA was carried out in water at 80 °C. The polymerization proceeded to high conversion, but the polymer molecular weight was twice as high as the predicted value ($M_n = 6 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.7$). It is possible to infer that the polymerization was somewhat controlled, but that very poor initiation occurred, possibly due to initiator hydrolysis. Lecomte et al. [170] have shown that MMA polymerization can also be carried out conveniently in aqueous suspension with $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ and CCl_4 as an initiator. In the absence of surfactants, bimodal distributions have been obtained due to diffusion limitations at high conversion. This problem has been overcome by adding a nonionic surfactant (Tween 80) that facilitates the dispersion of the polymer particles, resulting in a relatively narrow molecular weight distribution ($M_n = 3.25 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.55$) at high conversion.

Sawamoto has described the controlled radical polymerization of MMA using $[\text{RuCl}_2(\text{PPh}_3)_3]$ as a catalyst [218]. In organic solvents, this ruthenium catalyst [197] necessitates the use of an aluminum-containing co-catalyst, usually $\text{Al}(\text{O}^i\text{Pr})_3$, thus affording a very efficient control of the polymerization of methacrylic monomers. As the aluminum compound can not be used in neat water, polymerizations were initially carried out in a biphasic toluene:water 1:1 mixture. Polymerizations in this aqueous system were found to be somewhat faster than in neat toluene. In view of these results, the authors have demonstrated that aqueous polymerizations do not necessitate the use of any aluminum co-catalyst. Thus, in the absence of an aluminum salt, suspension polymerization of MMA in water at 80 °C was found to be efficient and controlled (83% conversion; $M_n = 9.6 \times 10^3 \text{ g mol}^{-1}$; $M_w/M_n = 1.42$).

ATRP in aqueous emulsion or suspension with copper-based catalysts has been the object of extensive research. Makino et al. [219] were the first to report MMA emulsion polymerization using CuBr/bpy as a catalyst and SDS as a surfactant. No living characteristics were observed, but it has later been shown that SDS interacts with the copper complexes to form a characteristic blue copper sulfate complex [185]. Early experiments by Matyjaszewski et al. [185] demonstrated that butyl methacrylate can be polymerized in emulsion using dNbpy and dAbpy ligands in combination with CuBr . The polymerization was found to be controlled, as evidenced by linear evolution of molecular weights with conversion, and by narrow molecular weight distributions. For example, 89% conversion was achieved after 75 min, yielding a polymer of $M_n = 2.82 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.26$ ($M_{\text{nth}} = 2.52 \times 10^4 \text{ g mol}^{-1}$).

Utilization of other ligands, such as $\text{Me}_6\text{-TREN}$, afforded ill-defined polymers. Careful elucidation of the polymerization mechanism by Matyjaszewski et al. [220] revealed that the partitioning of $\text{CuBr}_2/2\text{dNbpy}$ and $\text{CuBr}/2\text{dNbpy}$ between the apolar organic phase and the aqueous phase is crucial. Despite the hydrophobicity

of the ligand dNbpy, the catalyst, both in its Cu^{I} and Cu^{II} form, is partially soluble in water under the polymerization conditions. In a mixture of water/butyl methacrylate, up to 90% of Cu^{II} /dNbpy is present in the aqueous phase – the Cu^{I} /dNbpy species being much less water soluble. This indicates that catalyst diffusion through the aqueous phase is possible.

It must be noted that, even with an extremely hydrophobic catalyst, catalyst-free particles would be formed by radical exit and nucleation of new particles, and thus uncontrolled polymerization would occur. On the other hand, it is also proposed that with more hydrophilic ligands (such as $\text{Me}_6\text{-TREN}$, or pentamethyl diethylenetriamine (PMDETA) [221]) all the catalyst is located in the aqueous phase, and uncontrolled polymerization occurs in the hydrophobic polymer particles. However, these ligands are also ineffective in controlling the aqueous polymerization of *water-soluble* monomers (see above), hinting that ligand dissociation might also occur in these systems [215].

In addition to a proper choice of ligand hydrophobicity, the surfactant used is also critical. In general, non-ionic surfactants were found to be efficient for colloidal stabilization of the polymer particles [221]. This is to be expected, as, owing to the ionic nature of the catalyst, and the corresponding ionic strength, electrostatic stabilization is likely to be poor. Adequate hydrophilic/lipophilic balance (HLB) [222] is also a necessary criterion to ensure latex stability in ATR emulsion polymerization [223]. For the controlled polymerization of MMA, catalyzed by CuBr/dNbpy , an HLB of 17 was found to be optimal, and for the polymerization of butyl methacrylate, stabilization was optimal with surfactants Brij98 ($\text{H}_{35}\text{C}_{18}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$) (HLB=15) and Tween80 (polyoxyethylene sorbitan monolaurate) (HLB=15) [220]. Nevertheless, the colloidal stability of the formed latex is usually poor, even at low solid contents (15%) and in the presence of large amounts of surfactant (10%). Similar results were reported by Chambard et al. [224] for MMA polymerization using CuBr/dNbpy . The polymerization is controlled, as shown by linear evolution of M_n versus conversion, but at 60% conversion a low-molecular weight tail in the GPC trace appears that results from “dead” polymer formed by termination reactions. Most of these problems were alleviated through the use of a miniemulsion technique (see Section 7.1.1), as shown in the ATRP of butyl methacrylate with CuBr/dNbpy [225]. The miniemulsion recipe used employed hexadecane (10% in volume relative to monomer), as dNbpy is not hydrophobic enough to prevent Ostwald ripening, and the mixture was sheared by means of sonication. Sonication generates droplets with sizes of down to 300 nm, allowing for the preparation of stable latexes. In addition, the molecular weight of the polymer increases linearly with conversion, but the initiation efficiency is moderate. The found molecular weight ($M_n = 3.0 \times 10^4 \text{ g mol}^{-1}$, at 90% conversion achieved after 2 h at 70°C) is somewhat higher than the theoretical value ($M_{\text{nth}} = 2.4 \times 10^4 \text{ g mol}^{-1}$). The authors hint that escape of Cu^{II} species from the miniemulsion droplets occurs, resulting in a slightly increased termination.

Copper-based ATRP in emulsion has been achieved successfully under reverse ATRP conditions, where one starts with a conventional free radical initiator and $\text{CuBr}_2/\text{dNbpy}$ as a catalyst [226]. Typical commercial water-soluble free radical initiators such as potassium peroxydisulfate (in a phosphate buffer, $\text{pH}=7$), 2,2'-azo-

bis(2-amidinopropane) dihydrochloride (commonly designated as V50) or 2,2'-azobis[2-(imidazol-2-yl)propane] dihydrochloride (V44) can be used. The reaction requires an initial induction period of up to one hour, which corresponds to the time required for the initiator to decompose, forming deactivated radicals before reaching the atom transfer equilibrium (Scheme 7.11). Molecular weights increase linearly with conversion, and molecular weight distributions are as narrow as 1.2, but the initiation efficiencies are very low (typically between 0.1 and 0.4), resulting in a mismatch between experimental and theoretical molecular weights. This is attributed to irreversible early radical termination in the aqueous phase, where not enough Cu^{II} spin trap is present.

Finally, it has recently been reported that aqueous ATRP can be carried out conveniently in water in the presence of cyclodextrins [227]. Complexation by a randomly methylated β -cyclodextrin rendered the catalyst CuBr/dNbpy fully water soluble, and allowed for the controlled polymerization of MMA at 80 °C in water. Due to the presence of the cyclodextrin, the monomer too is water soluble, but the PMMA polymer formed ($M_n = 3.8 \times 10^4 \text{ g mol}^{-1}$, $M_w/M_n = 1.3$) is insoluble. In this respect, this type of polymerization is akin to a precipitation polymerization. Further growth of a styrene block on the PMMA chain is possible, albeit the blocking efficiency was limited.

7.4

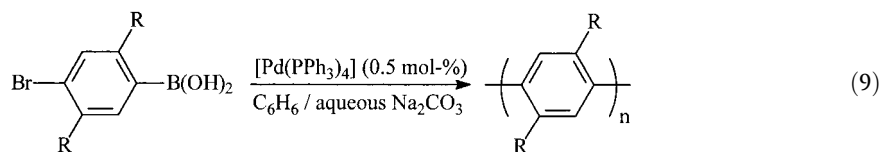
Polymerization by Suzuki-Coupling in Aqueous Systems

Transition metal catalyzed coupling reactions of aromatic halides, such as Heck or Suzuki coupling, are used extensively for the synthesis of low-molecular-weight organic compounds. With bifunctional substrates, polymers can be obtained. By contrast to all other polymerization reactions considered in this chapter, such reactions represent step-growth-type polymerizations.

The C-C coupling of aromatic halides usually requires the addition of a base in stoichiometric amounts, and the most common Brønsted bases are water soluble and can be employed conveniently in biphasic aqueous/organic systems.

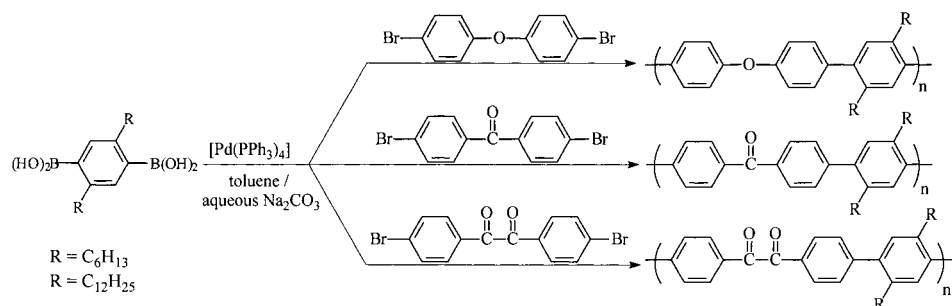
Suzuki coupling, the palladium-catalyzed cross-coupling of aryl or vinyl halides with organoboronates, is employed widely in organic synthesis. The reaction is most often carried out in an organic solvent (benzene) in the presence of a base [228]. Because of the reasonable stability of boronic acids and esters towards hydrolysis, Suzuki coupling can also be carried out in aqueous media. An extensive study of the reaction has shown that similar results are obtained in aqueous and non-aqueous systems [229].

The use of Suzuki coupling for the synthesis of polyphenylene polymers was introduced by Rehahn, Schlueter and Wegner [Eq. (9)] [230]. Poly(*p*-2,5-di-*n*-hexylphenylene) was prepared in a biphasic mixture of benzene and water as a reaction medium, using sodium carbonate as a water-soluble base. This AB-type polymerization afforded polymers containing, e.g., an average of about 28 phenylene units.



(e.g. R = H, CH₃, (CH₂)₃CH₃, (CH₂)₂C(CH₃)₃, ⁿC₈H₁₇, ⁿC₁₆H₃₃)

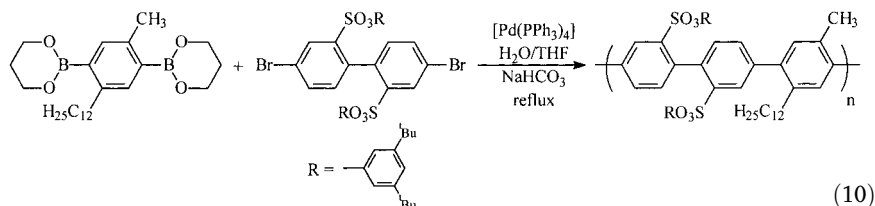
This method is applicable to a variety of alkyl-substituted phenylene AB-type monomers [Eq. (9)] [231]. The procedure was also extended to the condensation of AA and BB monomers (Scheme 7.12) [232].



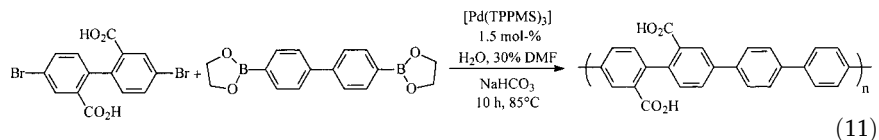
Scheme 7.12 Synthesis of functionalized poly(*p*-phenylene) via AA/BB Suzuki coupling in an aqueous biphasic system.

Hereby, poly(*p*-phenylene) polymers containing ether and carbonyl linkages in the polymer backbone are accessible. By polymerization of the AB₂ monomer 3,5-dibromobenzene boronic acid in a biphasic aqueous/organic medium, Kim and Webster obtained hyperbranched polyphenylenes [233]. Suzuki polycondensation in aqueous systems has proven to be a versatile method, which has been applied to the synthesis of various polymer types [234].

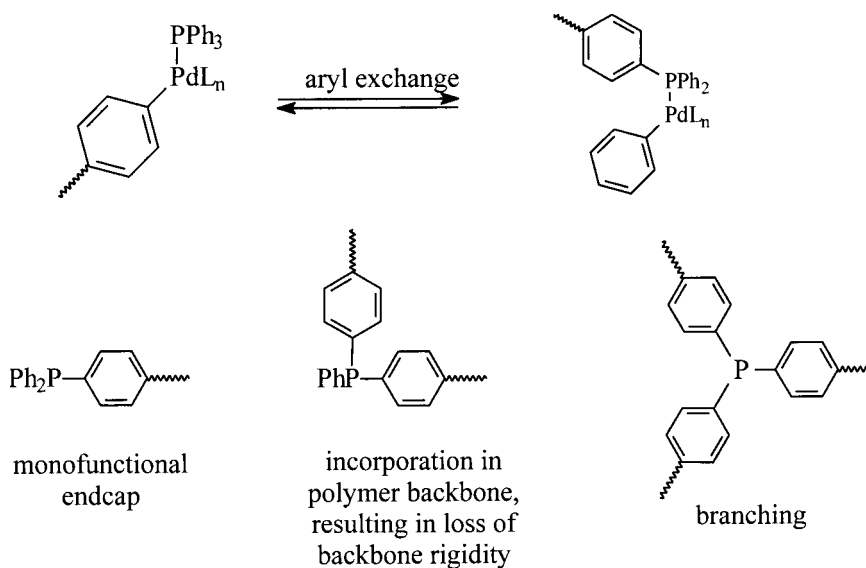
Polymerization in a single-phase homogeneous solution in THF/water mixtures (2:1) has also been reported [235]. Such reactions allowed for the preparation of a poly(*p*-phenylene) with sulfonate ester and dodecyl side groups [Eq. (10)]. By comparison to the aforementioned biphasic polymerizations, the synthesis of polymers with higher degrees of polymerization was reported in the solution procedure.



Polymerization via Suzuki coupling in aqueous solution was first reported by Novak et al. [Eq. (11)] [236]. A water-soluble catalyst precursor, $[\text{Pd}(\text{TPPMS})_3]$ ($\text{TPPMS} = 3\text{-Ph}_2\text{PC}_6\text{H}_4\text{SO}_3\text{Na}$) was employed. The resulting polymer is water soluble, and has a weight average molecular weight on the order of $5 \times 10^4 \text{ g mol}^{-1}$.



In later reports, Novak et al. pointed out that, as for traditional Suzuki coupling in non-aqueous organic solvents, the aqueous Suzuki coupling reaction is accompanied by side reactions that strongly affect the structure of the resulting polymer.



Scheme 7.13 Effect of aryl-aryl exchange in polymerization by Suzuki coupling, and modes of incorporation of phosphorus in the polymer.

First, a strong inhibition of the oxidative addition of aryl halide to Pd^0 by the coordination of the phosphine has been reported to be the source of slow kinetics [237]. Accordingly, when using phosphine-free catalyst precursors such as $\text{Pd}(\text{OAc})_2$, $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ or $[\text{Pd}_2(\text{dba})_3] \cdot \text{C}_6\text{H}_6$ ($\text{dba} = \text{dibenzylidene acetone}$) for Suzuki coupling (to prepare low-molecular-weight compounds) activities are an order of magnitude higher by comparison to polymerization with $[\text{Pd}(\text{aryl})\text{I}(\text{PPh}_3)_2]$ [237]. However, their use in polymerization has not been reported to date, perhaps due to a low stability of the active species, which is prone to decomposition to Pd black. Another side

reaction that has been studied with non-sulfonated triarylphosphines is the aryl-aryl interchange reaction in $[\text{Pd}(\text{aryl})\text{IL}_2]$ complexes (Scheme 7.13) [238].

In a typical organic synthesis by means of Suzuki coupling of monohalogenated compounds with monoalkyl boronic esters, this reaction results in the formation of small amounts of side products. In AA-BB step polymerization, however, this reaction represents a chain termination step or even results in branching (Scheme 7.13) [239]. Accordingly, with $[\text{Pd}(\text{aryl})\text{I}(\text{PPh}_3)_2]$ as a catalyst precursor in a THF/water mixture, the reaction results in the production of medium molecular weight polymer ($M_n = 9.7 \times 10^4 \text{ g mol}^{-1}$) that is not a rigid rod. This polymer contains a significant amount of phosphorus incorporated into the backbone; thus, chain termination through phosphine-aryl exchange must have occurred to a significant extent. Using a catalyst with more bulky phosphine ligands, $[\text{PdI}\{\text{P}(\text{o-tolyl})_3\}_2]$, for which the rate of aryl exchange is significantly lower, a higher molecular weight polymer is formed ($M_n = 2.0 \times 10^5 \text{ g mol}^{-1}$), and no phosphorus can be detected in the polymer. Conformational analysis of the polymer by light scattering and viscosimetry indicate that the resulting polymer is close to a rigid rod.

7.5

Conclusions and Outlook

Although the possibility of carrying out catalytic polymerizations in the presence of water had been known since the 1960s, significant advances in catalytic polymerizations in aqueous systems have only been achieved over the past decade. Today, (1) various different types of transition metal-catalyzed polymerizations can be carried out efficiently in aqueous systems. (2) A variety of polymers, ranging from hydrocarbons to water-soluble polymers, and a scope of polymer architectures are accessible. (3) Polymerization can be carried out in a controlled fashion. (4) Synthesis of polymer latexes possible in many cases.

One major thrust for these developments are certainly the recent discoveries of new late transition metal-based polymerization catalysts and initiators. Well-defined organometallic complexes, which do not require water-sensitive co-catalysts, are now available as catalyst precursors or initiators for olefin polymerization. Radical polymerization with metal complexes (ATRP) allows for a precise control of molecular weight in aqueous polymerization. An increased general concern with environmental issues makes water an attractive reaction medium. With polymer latexes, this advantage is not restricted to the polymerization process but also applies to the product itself. The general surge of interest in micro- and nanoparticles currently continues, and catalytic polymerization in aqueous emulsion provides convenient access to dispersions of a range of novel polymer nanoparticles in the size range of ca. 80 nm to 1 μm .

A number of issues and challenges will be of particular interest in the future. Up to now, little data is available regarding latex properties, such as stability and film formation, and on the properties of the resulting films (such as adhesion to substrates of varying polarity). In aqueous olefin polymerizations, these properties

can be controlled by copolymerizations of common monomers, including polar-functionalized olefins. Increases in catalyst efficiency regarding comonomer incorporation in ethylene polymerization and stability towards polar monomers are desirable. For instance, polyolefin latexes with film-forming properties could be useful for UV-stable coatings. The possibility of preparing a variety of different polymer architectures in aqueous polymerizations by ATRP, such as highly branched polymers, amphiphilic copolymers or surface-grafted inorganic or organic polymer particles, will be of strong future interest. Molecular weight control in the preparation of water-soluble polymers, such as polyacrylamide, is particularly attractive. Albeit very high catalyst activities have already been reported in some cases, for all of the polymerizations discussed further improvements in catalyst activities are desirable. For instance, in a polymerization aimed at preparing a latex it is desirable to leave the catalyst in the product in order to maintain the intriguing simplicity of this direct route to a polymer dispersion. To achieve negligible contents of more or less precious and potentially harmful metals and ligands, high efficiencies are necessary. The relevance of metal and ligand residues will obviously depend on the application sought and the catalyst used. The mechanisms of particle formation and polymerization kinetics are of fundamental interest in their own right, but an understanding is also desirable for a rational control of polymerization and to increase catalyst efficiencies in these multiphase systems in general. For instance, the location of the catalytically active metal centers during the different stages of the reaction (aqueous phase, inside monomer droplets and the respective polymer particles, or on the interface) is largely unclarified to date. The scope of particle morphologies accessible, e.g. core-shell particles with domains of different glass transition temperatures, remains to be explored.

In summary, recent advances in aqueous catalytic polymerizations have afforded a range of new materials, particularly polymer latexes previously inaccessible and new water-soluble polymers. Various attractive topics for fundamental research have in turn emerged, and potential applications can be envisioned. The attractiveness and versatility of this field results from the overlap and combination of polymer chemistry, organometallic chemistry, catalysis, and colloid science.

7.6

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8

Copolymerization of Carbon Monoxide with Alkenes

GIAMBATTISTA CONSIGLIO

8.1

Introduction

The copolymerization of alkenes with carbon monoxide has attracted the attention of chemists for many years [1]. Following the commercialization of Carilon, an alternating olefin carbon monoxide terpolymer based on ethene and small amounts (5–10%) of propene (Scheme 8.1, 1), by Shell [2, 3] in the 1990s interest in the identification of new and more active catalysts and of the stereochemical characteristics of the reaction has grown.

$$\text{X} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{C} \text{---} \end{array} \begin{array}{c} \text{R} \end{array} \right]_n \text{Y} \quad \mathbf{1}$$

End Group	Formation Reaction	
X = H-	$\text{L}_n\text{M} - \text{H} + \text{R} \text{---} \text{CH}=\text{CH}_2$	Initiation
X = H-	$\text{L}_n\text{M} \left[\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{C} \text{---} \end{array} \begin{array}{c} \text{R} \end{array} \right]_n + \text{H}^+$	Termination
X = R'OCO-	$\text{L}_n\text{M} - \text{COOR}' + \text{R} \text{---} \text{CH}=\text{CH}_2$	Initiation
Y = R'O- Y = R'O-CO-	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{C} \text{---} \end{array} \begin{array}{c} \text{R} \end{array} \right]_n \text{ML}_n + \text{R}'\text{OH} + \text{R}'\text{OH} + \text{CO}$	Termination
Y = -HC=CHR or -CR=CH ₂	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{---} \text{C} \text{---} \end{array} \begin{array}{c} \text{R} \end{array} \right]_n \text{ML}_n$	Termination

Scheme 8.1 Olefin-carbon monoxide copolymers: end-groups and reactions responsible for their formation.

Even after Shell announced the closure of their plant for Carilon production and despite the uncertain future of this commercial thermoplastic material, investigations are still being conducted. This is probably a consequence of the growing interest in catalysis by late transition metals for the polymerization and co-polymerization of olefins. Comprehensive reviews of this subject have appeared [4, 5] and will be taken as the basis for the following discussion.

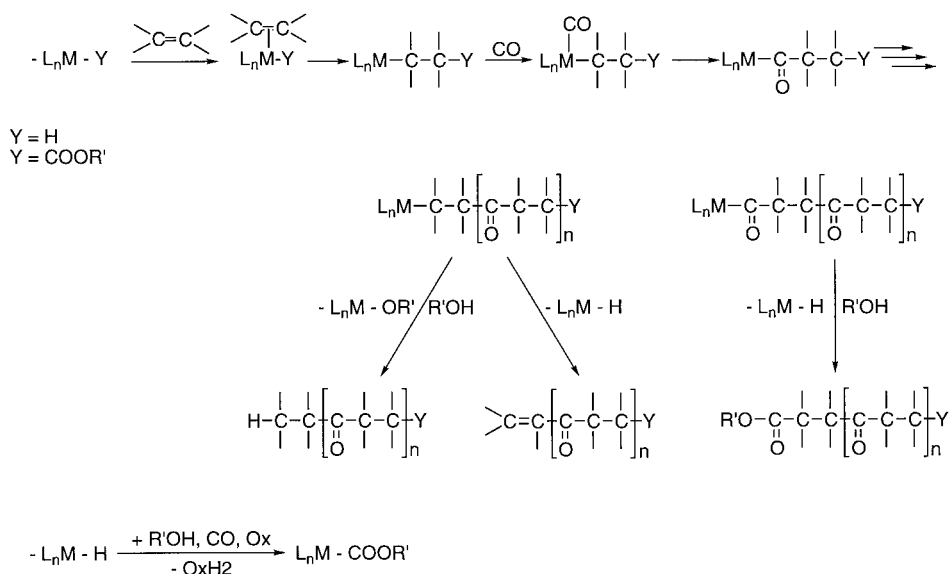
8.2

Copolymerization Catalysts and Mechanism

The aforementioned commercialization of Carilon was achieved after catalytic systems, active enough to incorporate propene and ethene into the macromolecules, were identified [3, 4]. The presence of small amounts of propene lowers the melting point of the polymer and enables processing of the material without degradation [6]. The catalytic systems used are complexes based on palladium of the type $[\text{Pd}(\text{L-L}')(\text{S})_2]\text{X}_2$ (where $\text{L-L}'$ { L= or L' } is a chelate ligand, S is a solvent molecule, and X is an anion with low coordination properties). These systems are usually employed in the presence of an oxidant (e.g., a quinone) to avoid the formation of inactive, reduced palladium species [7]. The catalytic species can be also formed "*in situ*" from their components, namely a palladium salt (typically the acetate), the ligand, and a strong acid that gives a non-coordinating anion. In general the corresponding $[\text{Pd}(\text{L-L}')(\text{S})(\text{CH}_3)]\text{X}$ or $[\text{Pd}(\text{L-L}')(\text{S})(\text{CH}_3\text{CO})]\text{X}$ compounds were used for mechanistic studies [8–11]. These species are considered to be useful models for the two propagating species during the catalytic process. As typical ligands for the copolymerization reaction of ethene and aliphatic olefins, diphosphines of the type $\text{Ar}_2\text{P}(\text{CH}_2)_n\text{PAr}_2$ were used, where the optimum value was n equal 3 and where Ar is equal to phenyl or *o*-methoxyphenyl [7, 12].

From the standpoint of the formation of the macromolecular chains, the identification of the end groups of the polymers is essential [7, 12–16]. Scheme 8.1 summarizes the identified chain end groups, as well as the reactions and the species responsible for their formation. The relative concentration of these groups changes according to the substrate and the nature of the catalytic system. Of the commonly found groups such as saturated hydrocarbyl, alkoxycarbonyl, and vinyl, only the latter can be assigned without alternative to terminating ends of the chain. The α -carbonylcarboxylate groups, which can probably also be assigned only to chain terminations, were identified for low molecular weight carbonylation products when the copolymerization reactions were carried out in the presence of a large excess of the oxidant [17]. Furthermore, labeling experiments using CH_3OD suggest that termination by methanolysis may involve an enolate-intermediate, which is formed by isomerization of the alkyl intermediate that is formed after ethene insertion [18].

Scheme 8.2 presents the mechanistic description of the formation of the macromolecules. Various pathways have been proposed to account for the first formation of the hydride-initiating species [4, 19].

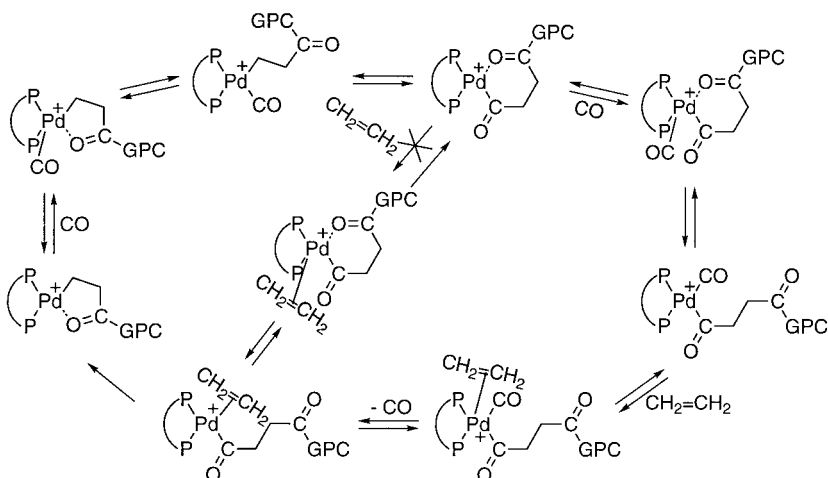


Scheme 8.2 Mechanistic description of the formation of the olefin-carbon monoxide copolymers.

In the copolymerization of ethene, for which unsaturated terminations have not been reported [7, 12], a variation in the ratio of the two alternative end groups as a function of the degree of polymerization was considered to indicate the existence of a two-phase polymerization system: a homogeneous catalytic site for growing chains of low molecular weights and a heterogeneous site, which results from the insoluble heavier growing chains.

The two migratory insertion steps, which are responsible for chain growing, were quantitatively studied, both theoretically and experimentally for systems modified by diphosphines. Qualitatively, it was concluded from the calculations that the lowest barrier is that pertaining to insertion within an ethyl carbonyl complex [20, 21], whereas, experimentally, olefin insertion within a dppp-Pd acyl-ethene complex shows the lowest barrier [10]. The reasons for the perfect alternation of the co-monomers were found in the thermodynamically disfavored double carbon monoxide insertion [22] and in the low coordination ability of ethene with respect to carbon monoxide accompanied by more rapid insertion of the latter within the alkyl intermediates [9]. “*In situ*” monitoring of the copolymerization of ethene and CO by PM-RAIRS (polarization modulation reflection absorption infrared spectroscopy) using solid $[Pd(dppp)(CH_3)(OSO_2CF_3)]$ as the starting complex (Scheme 8.3) suggested that the two different palladacycle intermediates represent two catalyst-resting states. For both, opening for the successive insertion is caused by carbon monoxide, as a result of the stronger coordination of this co-monomer [23].

In keeping with this complex mechanistic picture, the investigation of the reaction rate equation for the copolymerization of ethene, using $[Pd(dppp)(O_2CCF_3)_2]$,



Scheme 8.3 Proposed catalytic cycle for the growing steps of the CO-ethene copolymerization starting with $[\text{Pd}(\text{dppp})(\text{CH}_3)(\text{OSO}_2\text{CF}_3)]$ (GPC=growing polymer chain).

as a function of the activities of the two co-monomers, gave different results under different reaction conditions (Scheme 8.4) [24].

Kinetic modeling using an analogous tosylate complex was reported [25] and also depicts a complex mechanism. EXAFS studies on samples taken from the copolymerization mixture of ethene using $[\text{Pd}(\text{dppp})(\text{O}_2\text{CCF}_3)_2]$ as the catalyst precursor were interpreted according to the existence of five-coordinated catalytic intermediates (see Scheme 8.3) during the reaction [26].

$$v = a^a_{\text{cat}} \cdot a^b_{\text{CO}} \cdot a^c_{\text{Ethene}}$$

$$a = 0.83 \quad ([\text{cat}] = 1.10^{-4} - 2.10^{-5})^{\#}$$

$$b = 0.83 \quad a_{\text{Ethene}} = 0.065 \pm 0.01^{\#\#}$$

$$b = 0.31 \quad a_{\text{Ethene}} = 0.025 \pm 0.007^{\#\#\#}$$

$$c = 0.48 \quad a_{\text{CO}} = 0.014 \pm 0.002^{\#\#\#\#}$$

Reaction conditions: 200 ml CH_3OH , 85 °C, $\text{CF}_3\text{COOH}/[\text{Pd}]$ 24.8 $^{\#}$ $p(\text{CO})$ 45.9 bar, $p(\text{C}_2\text{H}_4)$ 45 bar, 1h; catalyst precursor $2.10^{-4} - 2.10^{-5}$ mol/L. $^{\#\#}$ Catalyst precursor $1.74.10^{-5}$ mol, $p(\text{C}_2\text{H}_4)$ 50 bar, 2.25 h; $p(\text{CO})$ 9.8-150 bar. $^{\#\#\#}$ Catalyst precursor $1.74.10^{-5}$ mol, $p(\text{C}_2\text{H}_4)$ 17 bar, 2.25 h; $p(\text{CO})$ 13.4-150.0 bar. $^{\#\#\#\#}$ Catalyst precursor $1.74.10^{-5}$ mol, $p(\text{CO})$ 46 bar, 2.25 h; $p(\text{C}_2\text{H}_4)$ 9.2-105 bar

Scheme 8.4 Kinetic equation obtained for the copolymerization of ethene with CO using $[\text{Pd}(\text{dppp})(\text{CF}_3\text{COO})_2]$ as the catalyst precursor.

8.3

Structure of the Olefin/Carbon Monoxide Copolymers

The possibility that olefin-carbon monoxide copolymers can exist in the isomeric poly-spiro ketal structure (Scheme 8.5) was recognized soon after the first synthesis of the copolymers of propene. Using dialkyl diphosphines as the modifying ligands [27], copolymers were obtained with blocks with the spiroketal form [28].

Scheme 8.5 Possible structures of olefin-carbon monoxide copolymers.



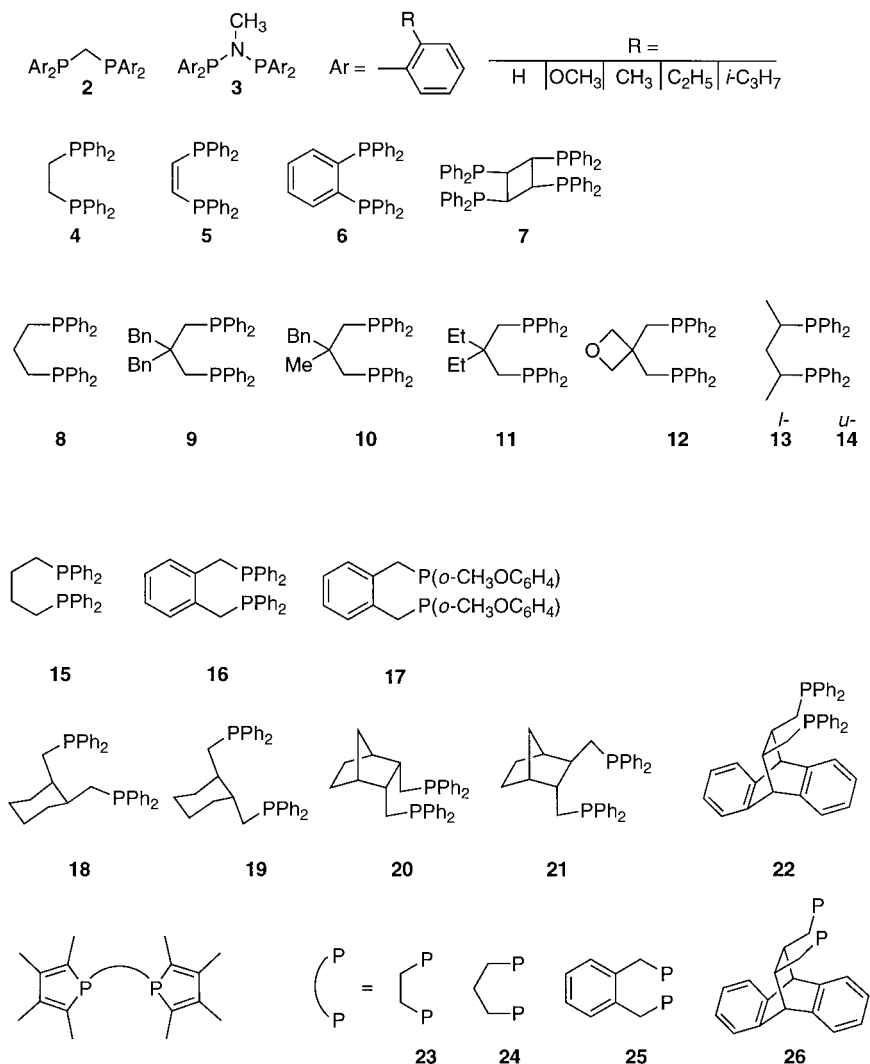
It is noteworthy that such basic ligands enable the production of regioregular copolymers with a prevalingly isotactic structure [15, 29]. However, only the use of chiral basic diphosphines, which enable the production of regio- and highly stereoregular copolymers [30], enabled the synthesis of materials with that structure only. This material dissolves in hexafluoroisopropanol to give the polyketone structure. First reports seemed to imply that the classical polyketone structure is the thermodynamically more stable one, at least for propene [28]. However, new reports seem to show that the difference in energy between the two structures is not very large [31].

The relative stability of the two structures seems to be determined by entropic factors. The increase in the size of the olefin substituent [32–35] or of the number of substituents, e.g., cyclic olefins such as norbornene [36] or dicyclopentadiene [4], leads to the stabilization of the spiroketal structure, which can survive even in solution. However, a precise determination of the relative stability has not been reported. As far as the growing of the copolymer chain is concerned, the mechanistic role, if any, of the spiroketal structure is still not very clear [4, 30]. It is noteworthy that the copolymers are, for the most part, isolated in the spiroketal structure when the copolymerization reaction is regio- and stereoregular.

8.4

Catalyst Precursors for the Copolymerization of Ethene

As far as the catalytic activity for ethene is concerned, the first systems investigated, which were based on triphenylphosphine as the ligand, showed rather low activity [37]. Among the chelating diphosphines of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, which ensure the correct geometry within the catalytic complex (see Scheme 8.3), the optimum ligand seems to be that having $n=3$ (dppp, **8**, Scheme 8.6) [7]. Turnover numbers as high as 10^6 mol ethene per mol of catalyst have been claimed. The activity of catalysts modified with a dinitrogen ligand (such as 2,2'-bipyridine or 1,10-phenanthroline), which are the systems used for the copolymerization of styrene [38], is lower. A



Scheme 8.6 Various chelate di-phosphorus ligands used for palladium-catalyzed carbon monoxide-ethene copolymerization.

beneficial effect of various metal acetates (such as cadmium or zinc acetates) on catalyst precursors formed from $\text{PdCl}_2/\text{dppp}/\text{CF}_3\text{CO}_2\text{H}$ has been reported [39]. Recent investigations demonstrated that the catalytic activity and the selectivity of $\text{Ar}_2\text{P}(\text{CH}_x)_n\text{PAr}_2$ ligands depends not only on the number of carbon atoms bridging the two phosphorus moieties, but also on the rigidity of that bridge and on the arene substituents on the phosphorus atoms. Unfortunately, the copolymerization experiments were usually carried out under different pressures and temperatures and the results are, thus, hardly comparable.

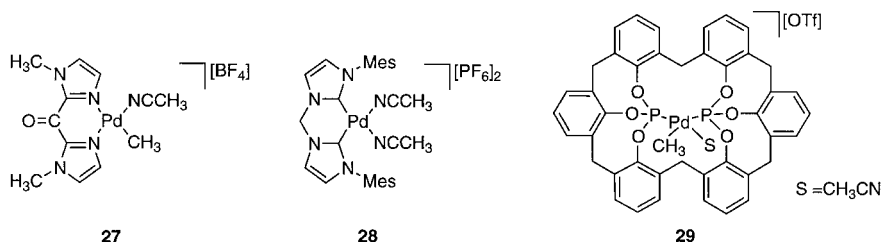
For both classes of four-membered chelate forming ligands (Scheme 8.6, **2** and **3**), the phenyl-substituted systems do not show essentially catalytic activity in the copolymerization of ethene in the presence of propene using palladium acetate and $\text{B}(\text{C}_6\text{F}_5)_3$ as the promoter and methylene chloride as the solvent. However, increasing the size of the R substituent leads to very efficient catalysts (turnover frequency up to $\sim 2 \times 10^4 \text{ mol (mol h)}^{-1}$ at 70°C). The incorporation of propene under the experimental conditions is more efficient for the methane-diphosphine **2** [40].

For the diphosphines that form a five-membered chelate ring (Scheme 8.6, **4**–**7**), increasing the rigidity of the backbone leads to an increase in the activity (e.g., one order of magnitude from **4** to **7**) [11]. The best turnover frequency reported at 85°C is close to $0.6 \times 10^4 \text{ mol (mol h)}^{-1}$ [41].

Several dppp-like ligands (which form a six-membered chelate ring), bearing different substituents on the carbon backbone (Scheme 8.6, **8**–**14**), were also used as palladium trifluoroacetate complexes [42] or bis-chelate complexes with various dinitrogen ligands [43]. Under identical reaction conditions (85°C), the trifluoroacetate complexes showed turnover frequencies in the range 1.5×10^4 – 0.7×10^4 , the highest activity corresponding to the *u*-ligand **14**. The *l*-ligand **13** was found to be $1.4 \times$ less active than its *u*-counterpart. The difference in reactivity was attributed to a subtle balance of steric and electronic effects (see also the copolymerization of propene). The catalytic activity of the bis-chelate complexes was somewhat higher. Various alkyl homologues of dppp were also used. The catalytic activity of the corresponding cationic bis(acetonitrile)complexes was somewhat lower than that of the parent dppp **8** [44]. Furthermore, supporting the dppp system on polysiloxane matrices leads to a loss of catalytic activity [45]. Hemilabile dppp homologues, with the general formula $\text{CH}_2\{\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{OR})_2\}_2$, on the other hand, showed comparable catalytic activity depending on the substitution [46]. Activation of $[\text{Pd}(\text{dppp})(\text{O}_2\text{CCH}_3)_2]$ with alumoxanes [47, 48] and $\text{B}(\text{C}_6\text{F}_5)_3$ [49] has been reported. Cationic palladacycles with the general formula $[\text{Pd}(\text{P}-\text{P})\{\text{o-C}_6\text{H}_4(\text{CH}_2\text{NR}_2)\}_2][\text{X}]$ (where P–P is dppp **8** or **9**) were found to be very active catalyst precursors (turnover number $\sim 6 \times 10^5 \text{ mol mol}^{-1}$) [50].

The catalytic activity of dppb **15** containing catalysts for ethene was reported to be about 2.6 times lower than that of the analogous dppp **8** catalysts [7]. Again, the use of more rigid systems (Scheme 8.6, **16** and **17**) [51, 52] was reported to be beneficial. Ligand **17** was about four times more active than the corresponding 1,3-bis(di-*o*-methoxyphenylphosphino)propane [52]. The catalytic activity of the other C_4 -bridged diphosphines **18**–**22** (Scheme 8.6) is lower. Ligand **18** has the highest activity (turnover frequency $\sim 0.6 \times 10^3 \text{ mol (mol h)}^{-1}$); the unusual selectivity of **21**, as well as of the *trans*-homologue of **22**, is remarkable, causing the preferential formation of methyl propanoate under the same reaction conditions [53, 54]. Palladium acetate complexes of the tetramethylphosphole ligands (**23**–**26**) in the presence of methanesulfonic acid have also been tested. Whereas **23** was inactive towards copolymerization, **25** showed turnover frequencies close to $0.8 \times 10^3 \text{ mol (mol h)}^{-1}$ at 90°C [55].

Catalyst precursors modified with other types of ligands, such as bis(*N*-methylimidazole) **27** [56], *N*-heterocyclic carbene chelates **28** [57], and calix[6]arene-derived



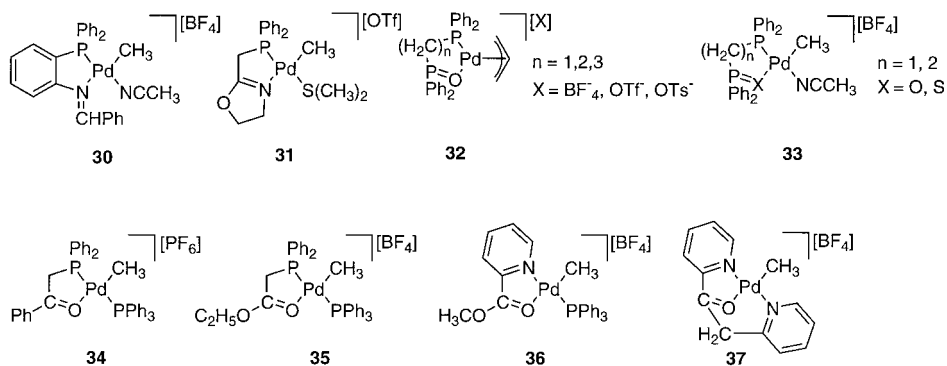
Scheme 8.7 Some catalyst precursors used for palladium-catalyzed carbon monoxide–ethene copolymerization.

diphosphites **29** [58] (Scheme 8.7), have also been used. The turnover frequencies were up to about 0.5×10^3 , 0.4×10^3 , and 5.3×10^3 mol (mol h) $^{-1}$, respectively.

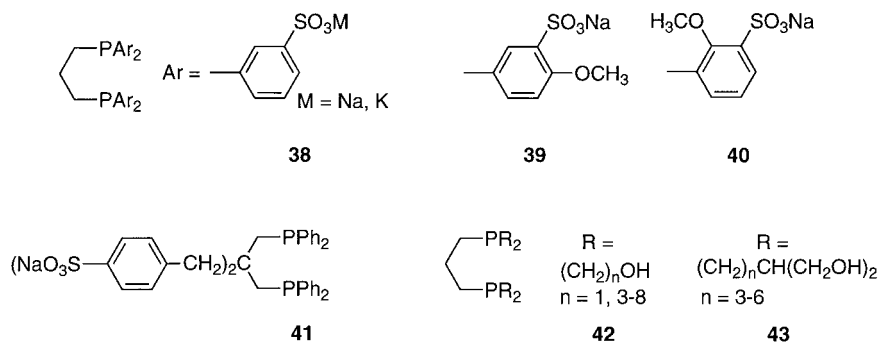
Heteroditopic ligands have been also proposed for the copolymerization reaction. The catalytic activity of systems containing one phosphorus ligating moiety is lower than that of the diphosphines. For the imine-phosphine-modified catalyst precursor **30** (Scheme 8.8), a low turnover frequency of 6 mol (mol h) $^{-1}$ [59] has been reported. Complex **30** was also used to investigate olefin and carbon monoxide insertions [60].

As a consequence of the living nature of the copolymerization with this catalyst, palladium-capped block copolymers of norbornene and ethene as well as of norbornene, ethene, and styrene were synthesized [61]. Higher activities (up to ten times higher) were observed for a series of oxazoline-phosphine complexes (e.g., **31**). Several complexes, modified with bisphosphine monooxide and monosulfide ligands (Scheme 8.8, **32** and **33**), were also used as catalysts precursors. The best reported turnover frequency is $\sim 0.6 \times 10^3$ mol (mol h) $^{-1}$ at 80 °C [62, 63]. A slightly lower activity was observed for the ketophosphine containing catalyst precursor **34** [64]. The activity of catalyst precursors **35**, **36**, and **37** is even lower [65].

Various water-soluble diphosphine ligands have been used for the copolymerization reaction or for the terpolymerization with propene (Scheme 8.9).



Scheme 8.8 Various palladium catalyst precursors modified with hybrid ligands for the carbon monoxide–ethene copolymerization.



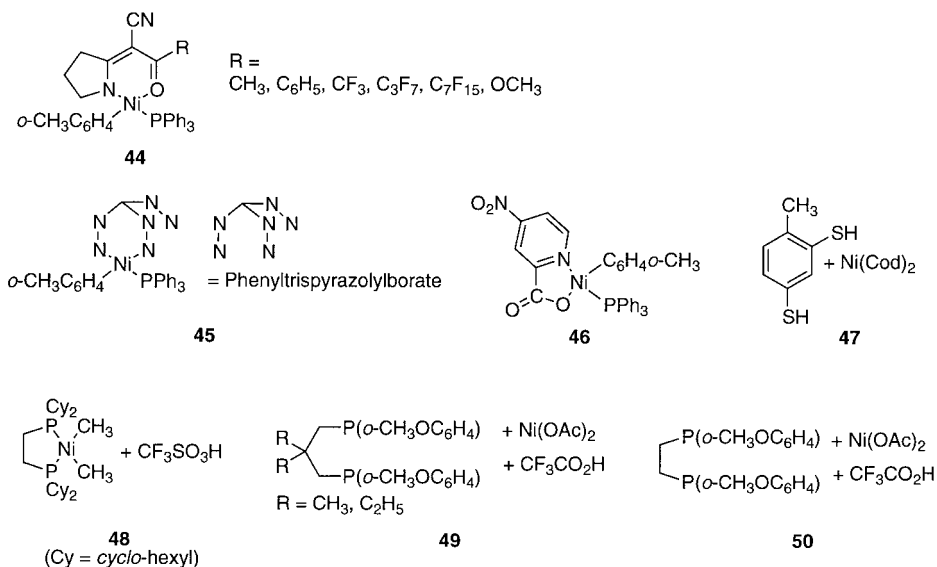
Scheme 8.9 Various water-soluble ligands used for palladium-catalyzed carbon monoxide-ethene copolymerization.

Previous experiments carried out with ethene using **38** ($M=K$) [66] had revealed a low catalytic activity, possibly due the rather impure ligand [67]. In the presence of Brønsted acids, such as trifluoroacetic or *p*-toluenesulfonic acid **38** ($M=Na$) showed turnover frequencies up to $7.6 \times 10^3 \text{ mol (mol h)}^{-1}$ at 70°C [68]. The anisyl systems **39** and **40**, the former with turnover frequencies up to $2 \times 10^5 \text{ mol (mol h)}^{-1}$, were even more active [69]. The productivity of **41** is somewhat lower ($\sim 1.4 \times 10^4 \text{ mol (mol h)}^{-1}$ at 85°C). Depending on the reaction conditions, the activities of systems **42** and **43** may be even higher than that of **38** [44].

The substitution of nickel for palladium catalyst precursors has, in principle, two advantages: the lower price of the metal and the lower tendency to plate. The effectiveness of nickel in the carbonylation of ethene to low molecular weight polyketones has been known for a long time [4]. Only recently, however, have nickel catalyst precursors with a reasonably high catalytic activity been discovered. The newest compounds are nickel complexes, which are modified by semicorrine-type ligands (Scheme 8.10).

Turnover numbers close to $1.2 \times 10^4 \text{ mol mol}^{-1}$ at 60°C were obtained with **44**, $R=C_3F_7$ or C_7F_{15} [70]. These catalysts are much more efficient than the previously reported nickel-phenylpyrazolylborate complex **45** [71], nickel-pyridine carboxylate **46** [72], and nickel-dithiophenol derivatives **47** [73]. Catalyst precursors **48** [74], **49** [74], and **50** [75] have been reported in the patent literature, the most active being **48**, with a turnover frequency of $8.7 \times 10^3 \text{ mol (mol h)}^{-1}$ at 80°C . Model studies using $[\text{Ni}(\text{dppp})(\text{S})(\text{CH}_3)]\text{X}$ and $[\text{Ni}(\text{o-MeOdppe})(\text{S})(\text{CH}_3)]\text{X}$ (**48**, Scheme 8.10) have revealed significant mechanistic differences with the analogous palladium system, the most important being the involvement of low-energy five-coordinated intermediates for the nickel catalysis [76].

Copper catalysts have also been mentioned as active for the copolymerization of ethene [77].



Scheme 8.10 Nickel-based catalyst precursors for the carbon monoxide–ethene copolymerization.

8.5

Copolymerization of 1-Olefins

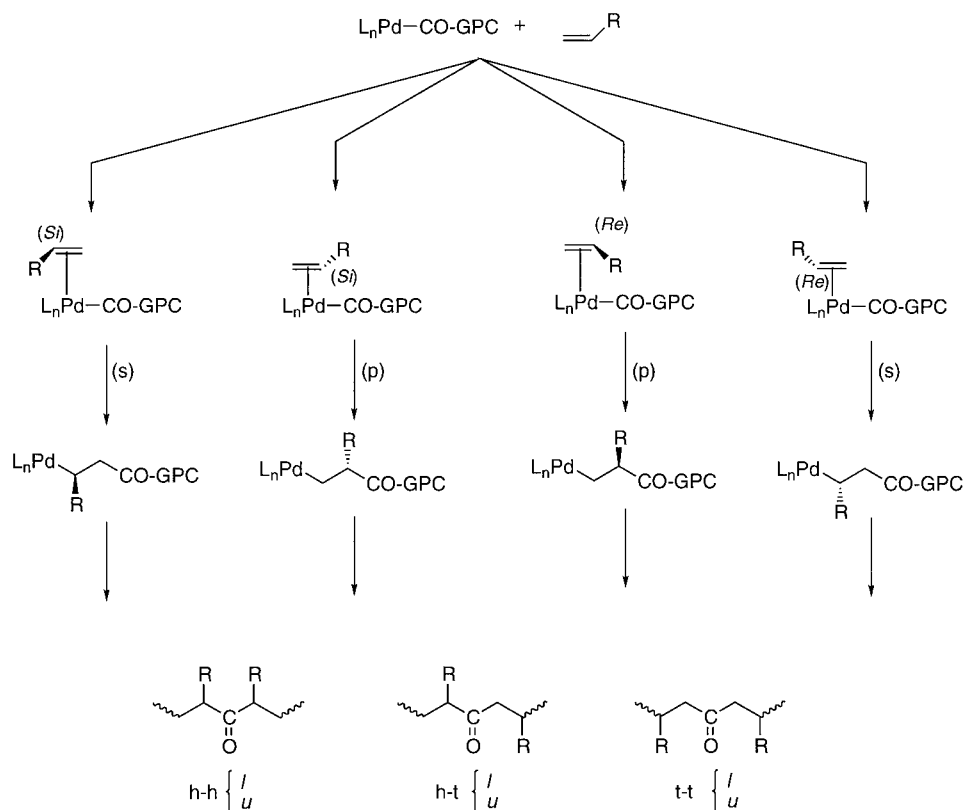
When 1-olefins are used as the substrate for the copolymerization with carbon monoxide, different moieties can form due to the absence of symmetry elements relating to the two unsaturated carbon atoms and to the enantiofaces of the olefin substrate (four different insertion pathways) (Scheme 8.11) [29].

Accordingly, six different dyads can form, namely the head-to-head, head-to-tail, and tail-to-tail, each one with either an *l*- or *u*-relative absolute configuration [78]. The regiochemistry of the copolymers of aliphatic 1-olefins is easily identified by ^{13}C NMR in the region of the resonances of the carbonyl groups [29]. In the case of copolymers of styrene, both the regioregular (h-t) and irregular structures are accessible; all the limiting stereochemical structures (iso-, syndio-, and atactic) are known for the former. The syndiotactic structure is still missing for the corresponding aliphatic olefins. In the following discussion, aromatic (styrene) and aliphatic (mostly propene) olefins will be separately treated due to the different type of ligand used.

8.5.1

Copolymerization of Styrene (and Homologues)

The catalytic systems first disclosed in the patent literature for the copolymerization of styrene [4], namely those modified with 2,2'-bipyridine **51** (Scheme 8.12)

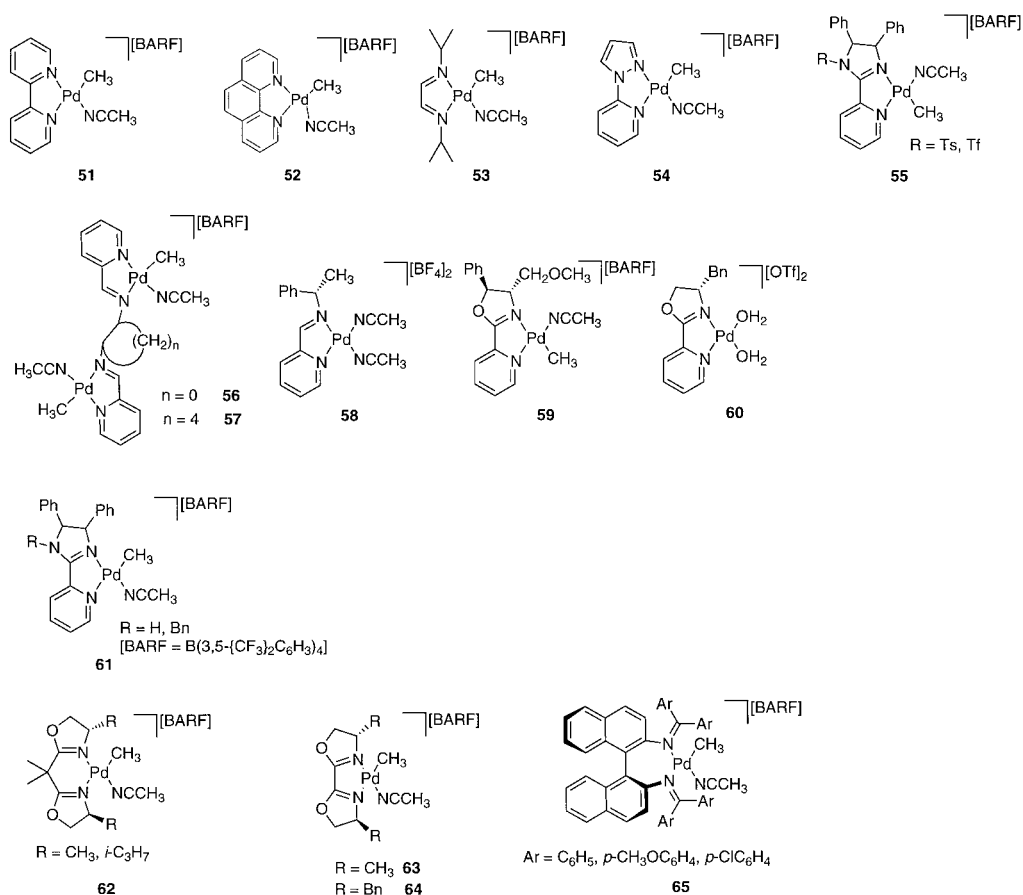


Scheme 8.11 Stereo- and regiochemistry during olefin insertion and consequent possible diads (the descriptors apply to propene; s=secondary, p=primary; GPC=growing polymer chain).

or 1,10-phenanthroline **52** were found to be largely syndiospecific (90% *u*-diads) [79] and completely regiospecific (secondary insertion of styrene) [8, 13].

The triad distribution in the copolymer was found to be bernoullian and is accounted for by a one-parameter model; therefore, chain end control of the stereochemistry was assumed [80]. For the systems based on bipyridine, no influence of the counter-ion on the stereochemistry of the produced copolymers was found; however, the catalytic activity was highest with the weakest coordinating anion [81]. Bis-chelated complexes of 2,2'-bipyridine or 1,10-phenanthroline [$\{\text{Pd}(\text{N}-\text{N})_2\}\{\text{X}_2\}$] were efficient catalyst precursors, particularly when used in 2,2,2-trifluoroethanol as the solvent [82]; under these conditions stabilization of the catalytic system by an oxidant is unnecessary, and very high molecular weights were obtained [83].

A better selectivity than with 1,10-phenanthroline (90% *uu*-triads) was obtained with 5-nitro-1,10-phenanthroline [84] and, more recently, with 1,4-diisopropyl-1,4-diaza-1,3-butadiene **53** [85]. Model studies with the latter catalytic systems have

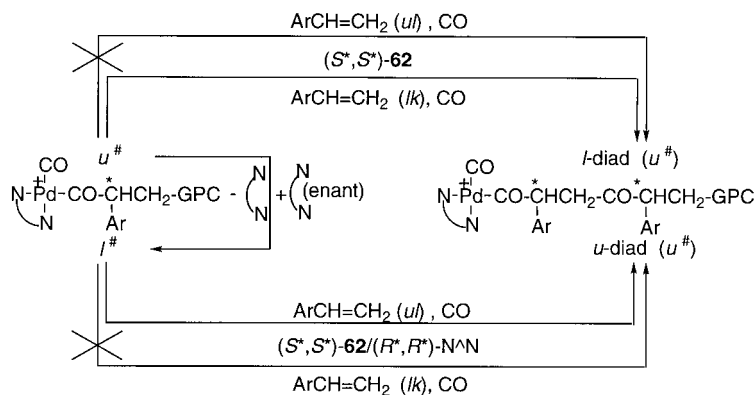


Scheme 8.12 Various palladium catalyst precursors modified with nitrogen ligands for carbon monoxide–styrene copolymerization (prevalingly syndiotactic (51–60), atactic (61), and isotactic (62–65)).

shown, however, low diastereoselectivity for the second styrene insertion. Analogously, 2-(1-pyrazolyl)pyridine **54** or the corresponding pyrimidine ligand gave a prevalingly syndiotactic copolymer ($\sim 85\%$ *u*-diads) [86]. The behavior of the pyridine-imidazoline systems using 4-*tert*-butylstyrene as the substrate is more unusual [87]. Whereas **55**, in spite of their chirality, gave copolymers with *u*-diads exceeding 82 to 85%, the analogous systems **61** gave largely atactic materials with a content of *l*-diads in the range 52 to 65%. It is noteworthy, however, that the geometry of the alkyl catalyst precursors **55** and **61** differs. The binuclear pyridine-imine complexes (**56** and **57**) both give a prevalingly syndiotactic styrene copolymer [88]. The low optical activity of the material prepared with (*R,R*)-**57** is consistent, however, with a larger concentration of *l*-diads with respect to **56**, as also shown by NMR spectroscopy on the two copolymers.

For the first experiments aiming to achieve isotactic copolymerization, optically active 2-pyridinecarboxaldehyde(1-phenylethyl)imine was used as the ligand (**58**); nevertheless, a prevalingly syndiotactic copolymer ($uu:lu:lu:ll$ -triads 56:20:20:4) formed [89]. The first truly isotactic styrene copolymers were obtained using catalysts modified with C_2 -ligands, namely 2,2'-propanediylbis(4-alkyl-4,5-dihydrooxazole) **62** [90] or with 2,2'-bi(4-alkyl-4,5-dihydrooxazole) **63** [91]. The copolymers showed a very high specific rotation which is consistent with a highly isotactic structure [34]. Similarly, chiral diketimines such as (*S*)-*N,N'*-bis(diphenylmethylene)-1,1'-binaphthyl-2,2'-diamine **65** gave highly isotactic copolymers, too [92]. The use of **62** under mild conditions enables the living isotactic copolymerization; after growing the isotactic fragments, addition of 2,2'-bipyridine to this system causes a switch and syndiotactic blocks are formed, because of the substitution on the catalyst of the chiral ligand by the achiral ligand. Thus, formation of a stereo-block copolymer is realized. The reverse procedure is clearly impossible. Remarkably, the use of **62** ($R=CH_3$) in the presence of one equivalent of the enantiomer of the free ligand leads to the formation of essentially syndiotactic copolymers [93]. To explain the latter result it is assumed (Scheme 8.13) that ligand exchange is rapid with respect to chain growth (facile ligand exchange was verified by NMR).

The intermediate $u^\#$ -complex (this relative absolute configuration refers to the ligand and to the center of asymmetry of the growing chain closest to the metal), which forms as a consequence of olefin insertion, is less stable than and transforms rapidly into the $l^\#$ -complex. The latter complex is more reactive towards ole-



u, l relative absolute configuration of two consecutive centers of asymmetry in the polymeric chain (i.e., name of the diad formed)

ul, lk relative topicity of the center of asymmetry of the growing chain closest to the metal and of the olefin enantioface to be inserted

$u^\#, l^\#$ relative absolute configuration of the ligand and of the center of asymmetry of the growing chain closest to the metal

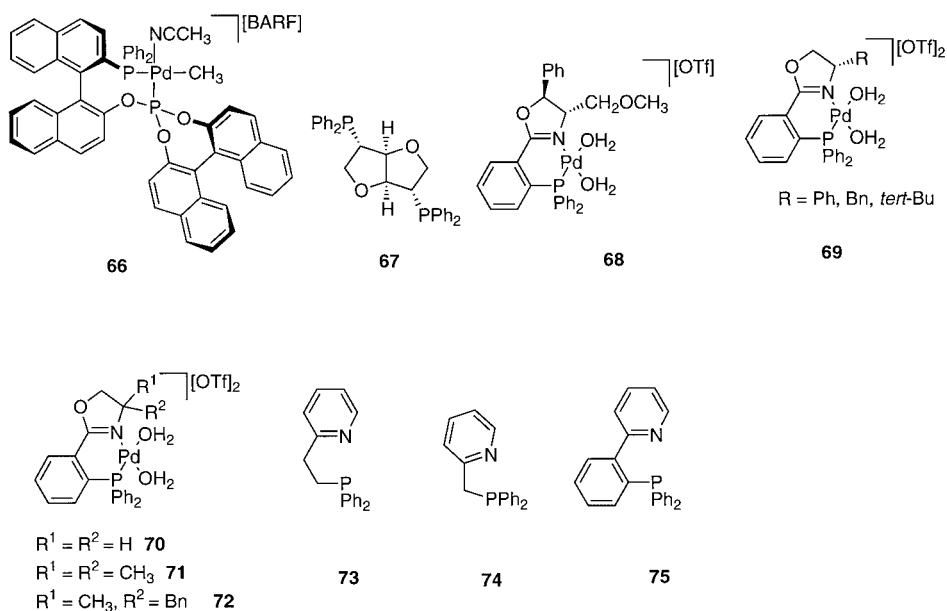
$N-N=2,2'$ -propanediyl-bis(4,5-dihydro-4-methyl)-2-oxazole

Scheme 8.13 Syndiotactic copolymerization of 4-*tert*-butylstyrene through enantiomorphic site control.

fin insertion; thus, enantiomorphic site control of the syndiotactic stereochemistry takes place.

The coordination lability of the above-mentioned bis-dihydrooxazole ligands, as demonstrated by the easy exchange reaction, causes decomposition of the catalytic systems at high carbon monoxide pressures (a few bars are enough). Phosphorus-modified catalytic systems are more promising in this respect. However, diphosphines and monophosphines ligands were found to produce low molecular weight ketones when styrene is the substrate [94] as a consequence of a rapid β -hydrogen elimination after secondary olefin insertion. Two notable exceptions are represented by the Binaphos system **66** [95] and, surprisingly, by the non-chelating diphosphine ligand Ddppi **67** [96] (Scheme 8.14). The latter system is the only one for which the styrene copolymer is isolated, at least partially, in the spiroketal structure [34].

As mentioned above and as demonstrated by model studies using various acetyl complexes, the insertion of styrene usually takes place with secondary regiochemistry [8]. However, styrene was found to insert with both primary and secondary regiochemistry into the metal-acetyl bond of a complex obtained by carbonylation of **66**. It is very remarkable that primary regiochemistry only was observed for the insertion in a homologous complex, in which a polyketone chain ($\text{CH}_3\text{CO}\{\text{CH}(\text{CH}_3)\text{CH}_2\text{CO}\}_{\sim 15}$) was substituted for the acetyl ligand. Thus, it was proposed that, for this catalytic system, primary insertion of styrene is responsible



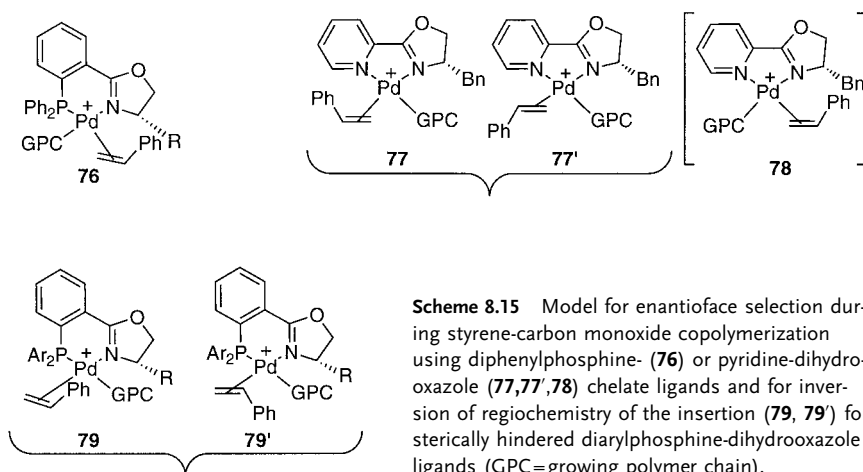
Scheme 8.14 Phosphorus-containing ligands (or their corresponding catalyst precursors) for carbon monoxide-styrene copolymeriza-

tion (prevalingly isotactic (**66–69**), atactic (**70–74**) and syndiotactic (**75**)).

for the growth of the chain and that secondary insertion leads to chain interruption due to rapid β -hydrogen elimination [95, 97].

Systems modified by hybrid P–N ligands (**68–75**) were also found to be active for the copolymerization of styrene. In contrast to the N–N ligand [8, 9], their productivity is increased by increasing the pressure of carbon monoxide. In the case of the phosphine-dihydrooxazole ligands (**68–72**) the geometry of the ligand is very important for the steric control. The presence of only one substituent on position 4 of the dihydrooxazole ring (e.g., **69**) is essential to achieve isotactic copolymerization [98]. Chirality associated with the presence of two different substituents in that position (Scheme 8.14, **72**) is not sufficient to cause efficient *l*-enantioface discrimination [99]. On the basis of these results, the model for styrene coordination (**76**) reported in Scheme 8.15 was assumed.

Remarkably, pyridine-dihydrooxazole ligands with the same chiral moiety as the previous ligands (compare **59** and **60** with **68** and **69**) produce prevailingly syndiotactic copolymers. The sign of the low optical activity of those copolymers, however, is consistent with the presence of small amounts of *l*-dyads, for which the same enantioface, as in the case of the corresponding P–N ligands, is prevailingly inserted (compare **78** vs. **76** in Scheme 8.15); however, intermediates **77** and **77'** alternatively, and not **78**, are prevailingly responsible for chain growth. Model studies on alkyl and acetyl complexes of these ligands are in keeping with this interpretation [100, 101]. It is remarkable that regioirregular styrene copolymers have become accessible by increasing the size of the arene substituents on phosphorus in the phosphine-dihydrooxazole ligands. According to the proposed model (Scheme 8.15), steric repulsion by those substituents and the growing chain would make a possible intermediate, similar to **76**, unfavorable, and would cause a change in the olefin coordination site as in **79** and **79'**. Again, steric repulsion between substituents on the double bond and on the arene causes a switch in the preferred regiochemistry towards **79** and **79'**.



Scheme 8.15 Model for enantioface selection during styrene-carbon monoxide copolymerization using diphenylphosphine- (**76**) or pyridine-dihydrooxazole (**77,77',78**) chelate ligands and for inversion of regiochemistry of the insertion (**79, 79'**) for sterically hindered diarylphosphine-dihydrooxazole ligands (GPC=growing polymer chain).

As far as the stereoregulation of the copolymers is concerned, the relative role played by the enantiomorphic site and the growing chain in the catalytic systems modified by the phosphine- and pyridine-dihydrooxazole ligands (see **59** and **68**) was investigated by studying the terpolymerization with ethene at low styrene concentrations [102]. For the phosphine-dihydrooxazole ligand (**68**), the chiroptical properties of the terpolymers normalized for the styrene content do not change appreciably with respect to the styrene copolymers, in keeping with the overwhelming role of the enantiomorphic site in the steric control of the copolymerization. In contrast, the normalized optical activity for the copolymer obtained with the pyridine-dihydrooxazole ligand (**59**) increases as a result of the decrease of the styrene content. This indicates an increase of the extent of enantioface discrimination following an increase of the ethene content of the terpolymer, in keeping with the production of the prevalingly syndiotactic copolymer with that ligand.

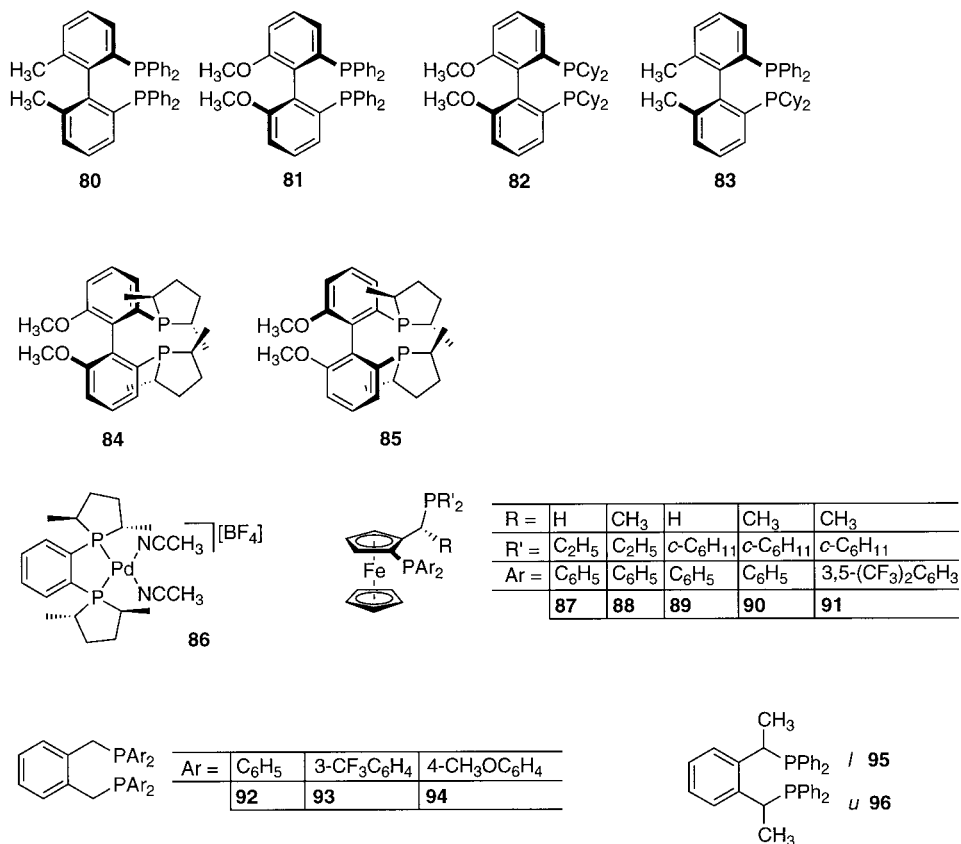
Furthermore, the phosphine-dihydrooxazole ligands show an unusual behavior with respect to ethene and styrene. The productivity of those systems is larger for styrene than for ethene under equal reactions conditions; nevertheless, in the terpolymerization experiments ethene, and not styrene, is prevalingly inserted. Considering that ethene was inserted more rapidly than styrene into model acetyl complexes [103], the “poisoning” effect of ethene can be explained by assuming that ethene is coordinated more easily, without rapid olefin dissociation, and that rate-determining carbon monoxide insertion into the two different alkyl intermediates occurs.

8.5.2

Copolymerization of Propene (and Other Aliphatic Olefins)

The first copolymerization reactions of propene using C_{2v} -symmetric catalytic systems, such as those modified by chelating bis(diphenylphosphine) (e.g., dppp, **8**, Scheme 8.6) or similar bis(diarylphosphine) ligands, showed a very low regioselectivity [4]. For dppp the concentration of the H-T moiety is about 56%; the stereoregularity is difficult to determine, but it is certainly very low [104]. High molecular weight copolymers [105] (or terpolymers with ethene), which are thermoplastic elastomers, can be prepared under controlled conditions with this catalyst [106]. With more basic ligands, i.e., dppp homologues containing alkyl groups such as ethyl, iso-propyl or cyclohexyl, we obtained essentially completely regioregular copolymers with a fair isotactic stereoregularity [29]. The stereoregularity is probably due to chain end control and arises from primary insertion of the olefin co-monomer [15]. Low regioselectivity and low stereoselectivity were also obtained with the C_2 -symmetric, fully aromatic atropisomeric ligands **80** and **81** (Scheme 8.16).

Substituting the phosphorus phenyl groups with alkyl groups (e.g., with iso-propyl or cyclohexyl **82**) causes a completely regioregular and highly isotactic copolymerization [16]. It is remarkable that the catalyst based on the C_s -symmetric ligand **83** also gave an essentially regular copolymer; however, in contrast to the other atropisomeric catalysts, this system shows an *ul*-relationship between the chirality descriptor of the copolymer and that of the ligand. Furthermore, the asymmetric catalyst



Scheme 8.16 Some phosphorus-containing ligands (or their corresponding catalyst precursors) used for carbon monoxide-propene copolymerization.

66 (Scheme 8.14) gave a regular isotactic copolymer [107, 108]. This system was also used for the isotactic copolymerization of various 1-olefins including functionalized substrates [109] and ω -perfluoroalkyl-1-alkenes [110]; furthermore, propene/4-*tert*-butylstyrene terpolymers were also obtained [111]. It is unclear as to why the (*R,S*)-(*c*-Pen)₂-Binaphos (the cyclopentyl-substituted homologue of Binaphos) gave a polyketone with the opposite sign of optical rotation than that obtained with (*R,S*)-Binaphos (**66**); the ethyl homologue gave an atactic copolymer [108].

The difference in behavior of the two diastereomeric ligands **84** and **85** (Scheme 8.16) was remarkable: whereas ligand **84** produced a completely regioregular but atactic copolymer with very high catalytic activity, **85** gave a completely regular isotactic copolymer with very low catalytic activity.

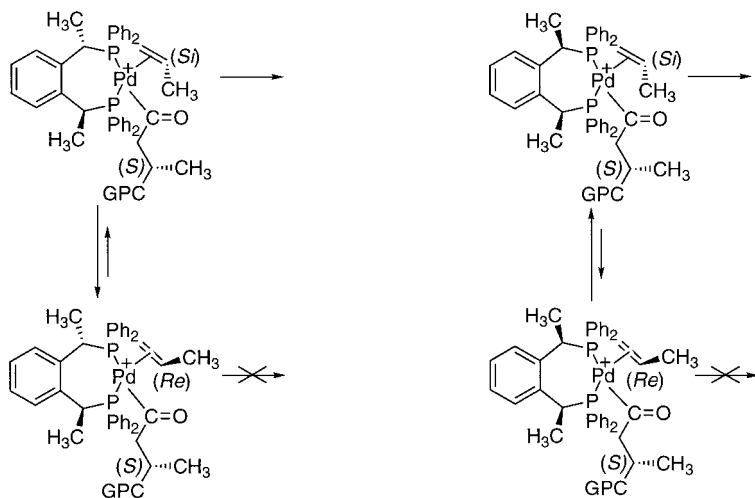
Despite the low activity of the system containing the dppe ligand (**4**, Scheme 8.6) for ethene copolymerization [7], the related Me-Duphos-modified catalyst **86** (Scheme 8.16) copolymerizes propene to isotactic copolymers with a fair catalytic

activity (turnover number $\sim 2.2 \times 10^3$ mol substrate per mol catalyst at 50°C in 23 h) [32]. The same system was recently used for functionalized olefins such as methyl *N*-(3-butenyl)carbamate, phenyl *N*-(2-propenyl)amide [112] and some vinyl epoxides [113]. Highly isotactic enantioselective copolymerization, however, with low catalytic activity (turnover frequency up to ~ 37 mol (mol h) $^{-1}$ at 45°C), with propene, 1-heptene or 1-octene as the substrate, was achieved with a catalytic system modified by Ddppi (**67**, Scheme 8.14) [34, 114]. Using the same system, functionalized olefins such as ω -undecenyl alcohol, ethyl and butyl acrylate were also copolymerized [34, 115]. The most active class of ligands identified so far for propene is that of the C_1 -symmetric ferrocenylphosphines **87–91** [116, 117]. Central and planar chirality, large substituents on the phosphorus bound to the asymmetric carbon atom, and aryl groups on other phosphorus atom containing electron withdrawing substituents (see ligand **91**) are all essential for high catalytic activity and regularity of the copolymers [117]. The first investigated ligand, josiphos (**90**), gave good results in the copolymerization of other olefins such as 1-butene, 4-methyl-1-pentene and various allylbenzenes [118].

As mentioned above for dppp **6**, diphenylphosphino-disubstituted chelate diphosphine ligands usually copolymerize propene to regio- and stereoirregular materials [104]. A notable exception was found in the 1,2-bis[(diphenylphosphino)methyl]benzene ligand **92**, for which irregularity is quite low [119]. This irregularity was further reduced when the aryl substituents contained electron withdrawing groups, such as **93**. According to the analysis of the low-molecular weight by-products, which are formed under conditions similar to those applied for the copolymerization reactions, ligands **93** and **94** insert propene with essentially reversed regiochemistry [119]. However, the copolymers formed with the two catalytic systems are quite similar with respect to stereochemistry (prevailing isotactic) and regiochemistry (about 98% content of the h-t enchainment).

It is very interesting that the stereochemistry of the ligand (C_2 vs. C_s -symmetry, **95** and **96**, Scheme 8.16) does not affect the stereochemistry of the produced copolymer, which is regioregular and isotactic in both cases; this is in sharp contrast to the behavior of zirconocene catalysts having the same symmetry for olefin polymerization [120] and to the trend observed in the polymerization of propene by nickel-diimine catalysts [121]. However, the reactivity of the meso-ligand **96** is about $84\times$ that of the rac-ligand **95** for propene, whereas the reactivity ratio is only 2.4 when ethene is used as the substrate. Similar but weaker effects were observed for diastereomeric **13** and **14** and for their *o*-anisyl-substituted homologues, for which, however, the copolymerization lacks regioselectivity. There is clearly an important steric contribution to the difference in reactivity due to the fact that propene has two enantiofaces. These results were rationalized by assuming the formation (Scheme 8.17) of the intermediate responsible for the growth of the chain (i.e., the intermediate for which there is a *l*-topicity between the growing chain and the coordinated olefin) in low concentration for the racemic ligand, possibly because of steric reasons [122].

Analogous to the case of styrene, the terpolymerization reactions of propene with ethene were carried out to identify the factors responsible for enantioface discrimi-



Scheme 8.17 Attempted rationalization of the higher catalytic activity of the *meso*- vs. the *rac*-ligand for carbon monoxide-propene copolymerization.

nation using catalysts modified with **81**, **82** and **90**. In particular for the regiospecific systems **82** and **90**, the optical activity of the terpolymers normalized to the propene content changes only very little with respect to the copolymers obtained with the same precursors catalyst, thus showing an overwhelming enantiosite control [123].

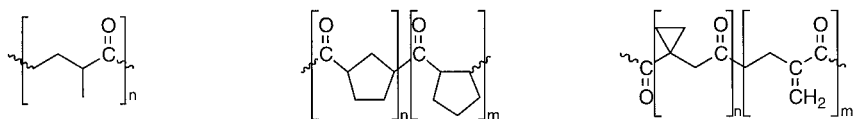
Various copolymers and terpolymers poly(ketone)s containing functional groups (phenolic or phenyl ether substrates) were prepared using $[\text{Pd}(\text{dppp})(\text{CH}_3\text{CN})_2](\text{BF}_4)_2$ as the catalyst precursor [124, 125]. Using the same catalytic system mesogenic 1-alkenes were also copolymerized [126].

8.6

Copolymerization of Internal and Cyclic Olefins

The copolymerization of internal olefins has received little attention, probably due to the lack of catalytic activity of the systems discussed so far. Only results concerning (*Z*)-2-butene have been reported. Using the Me-Duphos-modified catalyst **86** (Scheme 8.16), a poly[1-oxo-2-methyl-1,4-butanediyl] (Scheme 8.18) formed with low molecular weight (mean oligomerization degree ~ 7) [32].

The optical activity of the material suggested a prevailing isotactic structure. Similarly cyclopentene has received little attention [127]. This substrate gives copolymers with a prevailing 1,3-enchainment with respect to the normal 1,2-enchainment. The best regioselectivity ($\sim 95\%$) was obtained using (*R,R*)-[bicyclo[2.2.2]octane-3,4-diylbis(methylene)]bis(diphenylphosphine) as the modifying ligand. However, the largest molar masses (up to 8500) were obtained when the copolymers showed the greatest extent of 1,2-enchainment. A prevailing diisotactic structure has been suggested for the copolymers giving the most simple NMR spectra.

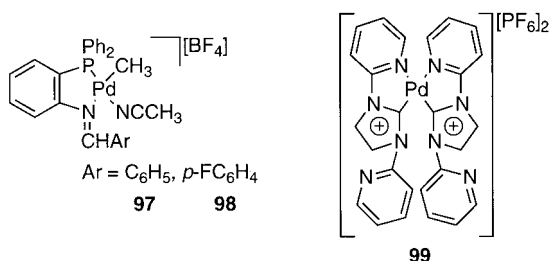


Scheme 8.18 Structure of the copolymer obtained from (Z)-2-butene, cyclopentene and methylenecyclopropane, respectively.

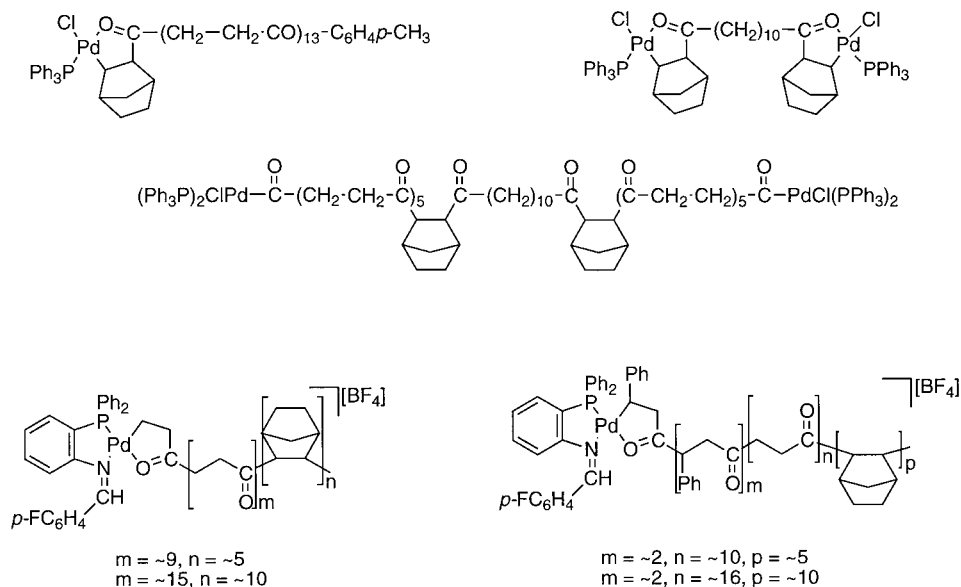
Copolymers of methylenecyclopropane were obtained using $[\text{Pd}(\text{dppp})(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$ as the catalyst precursor. According to IR and NMR analysis, the material contains both ring-opened and cyclic structures (Scheme 8.18) [128]. Terpolymers containing propene were also prepared with this catalyst precursor.

Copolymerization reactions of strained olefins, such as norbornene, norbornadiene and their derivatives, have been known for a long time; however, the polymerization degree is usually quite low. Using norbornene as the substrate, cationic $[\text{Pd}(\text{PPh}_3)_n(\text{CH}_3\text{CN})_{4-n}][\text{BF}_4]_2$ [36, 37] or neutral catalyst precursors $[\text{Pd}(\text{PPh}_3)_4]/\text{RX}$ (RX is e.g., β -bromostyrene) were first used and gave polymerization degrees of up to 4 and 17 respectively [129]. With a system formed *in situ* from $\text{Pd}(\text{OAc})_2/2,2'$ -bipyridine/*p*-TsOH, the copolymer (polymerization degree up to 15) was formed exclusively with a spiroketal structure as was reported for the dicyclopentadiene copolymers [4]. This system was modified slightly for the copolymerization of some norbornene derivatives and for norbornadiene; somewhat higher molecular weights have been reported [130, 131]. Terpolymers of styrene and norbornene were also obtained [132].

Other catalytic systems were used recently, namely a Ddppi system (**67**, Scheme 8.14) for dicyclopentadiene and di(methylcyclopentadiene) [96] and imino-phosphine complexes (Scheme 8.19, **97** and **98**) or hybrid terdentate carbene ligand complexes (**99**) [133] for norbornene. Furthermore, the copolymerization of various substituted norbornadienes and norbornenes has been achieved with $\text{Rh}_6(\text{CO})_{16}$ under water gas shift reaction conditions (55°C , water and 100 atm CO) [134].



Scheme 8.19 Catalyst precursors used for carbon monoxide-strained olefin copolymerization.



Scheme 8.20 Palladium-capped co-oligomers.

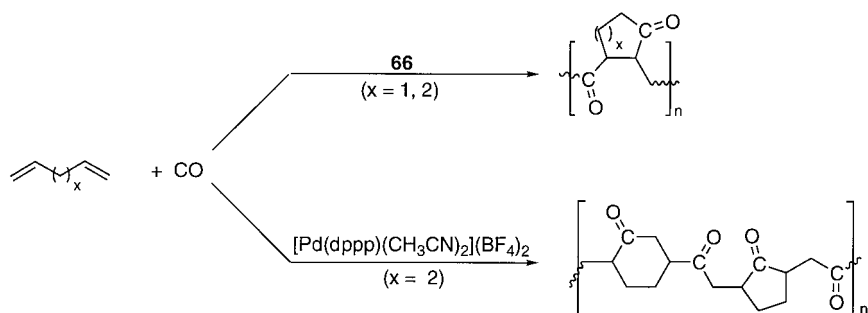
Taking advantage of the non-terminating nature of some of the catalytic systems, palladium-capped co-oligomeric compounds were also prepared (Scheme 8.20).

Living copolymerization of the electron-poor strained olefins diethyl bicyclo [2.2.1]hepta-2,5-diene-2,3-dicarboxylate and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate was achieved using palladium(II) neutral initiators such as iodo(*endo*-6-phenyl-2-norbornene-*endo*-5s,2p)(triphenylphosphine)palladium(II) [135]. Diblock copolymers of the two substrates were also prepared. Both the above-mentioned copolymers undergo retro Diels–Alder reactions to form poly (ketovinylene); the former material gave complete conversion only at a rather high temperature (280 °C).

8.6.1

Cyclocopolymerization of α,ω -Dienes

When α,ω -dienes are used as the substrate cyclocopolymerization proceeds if the two double bonds are separated by an adequate distance. Thus, whereas for 1,7-octadiene or 1,6-heptadiene-4-ol ring formation was not observed, cyclocopolymerization occurred in the case of 1,5-hexadiene and 1,4-pentadiene [128]. Using the (*R,S*)-Binaphos catalytic system **66** with both substrates results in a regiospecific (Scheme 8.21) but not diastereospecific reaction, since both *cis*- and *trans*-disubstituted rings are formed at around a 1:1 molar ratio [136].



Scheme 8.21 Regiospecific and regioselective cyclocopolymerization.

Similarly, the copolymerization of 1,5-hexadiene using a catalytic system modified with 1,3-bis(diisopropylphosphino)propane was also regiospecific; the diastereoselectivity was 3:1 in favor of the *cis*-relative configuration. In contrast, the catalytic system containing the dppp ligand **8** (Scheme 8.6) gives a copolymer containing both 5- and 6-membered rings in the polymer backbone (Scheme 8.21) [137]. The regiospecificity of the two former systems is assumed to arise from two primary insertions, in keeping with the results obtained for propene.

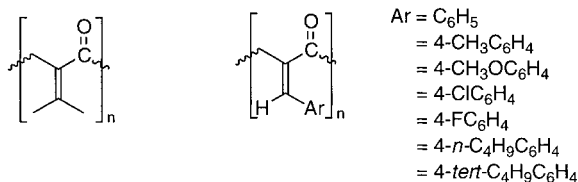
8.7

Conclusions

The alternating copolymerization of alkenes with carbon monoxide has been of great interest for the last twenty years, both from scientific and technological viewpoint. Expectations were high [2, 3, 106], but the production of Carilon on a large scale was later dismissed. However, there is still interest in the involved catalytic systems, probably because of the growing importance of Group 8 metals for polymerization processes [138] and of the outstanding properties of the copolymers [3].

Moreover, the copolymerization of other unsaturated substrates, such as the alkenes, has been reported. The alternating copolymerization of 1,1-dimethylallene with carbon monoxide was achieved using $[Pd(PPh_3)_2(CH_3CN)_2](BF_4)_2$ (Scheme 8.22). Chelate diphosphine-modified catalyst precursors resulted in a lack of activity [139]. Various arylallenes were copolymerized using $Rh[\eta^3-CH(Ar)C\{C(=CHAr)CH_2C(=CHAr)CH_2CH_2CH=CHAr\}CH_2](PPh_3)_2$ (where $Ar = p-CH_3OC_6H_4$) [140–142].

Very interesting transformations of the polyketones into other polymeric materials have been reported. An optically active isotactic poly[1-oxo-2-methylpropane-1,3-diyl] was reacted with methylenation reagents to give poly[1-methylene-2-methylpropane-1,3-diyl] [143] apparently without racemization. A similar material was reduced to the corresponding poly[1-hydroxo-2-methylpropane-1,3-diyl] with 40% *l*-diastereoselectivity using tetrabutylammonium borohydride [144]. Furthermore, ethene copolymers or ethene-propene terpolymers were transformed into



Scheme 8.22 Prevailing structure of copolymers of carbon monoxide with allenes.

the corresponding methoxyimines, which undergo α -substitution upon treatment with BuLi followed by addition of an electrophile such as methyl iodide [145]. Previously described transformations include conversion into the corresponding 1,3-dioxolane derivatives by reaction with diols to poly(ethenepyrroles) by condensation with primary amines and Baeyer-Villiger oxidation.

8.8

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9

Strategies for Catalytic Polymerization of Polar Monomers

AYUSMAN SEN* and MYEONGSOON KANG

Abstract

The coordination of the functionalities that may be present either in the monomer or in the growing polymer chain to the metal center is one key impediment in the development of new transition metal-based catalysts for the insertion polymerization of polar monomers. On the other hand, rapid β -halide abstraction has prevented metal-catalyzed polymerization of vinyl halides. Several examples are discussed to illustrate these problems.

9.1

Introduction

Polyolefins with a high density of functional groups along the backbone are of great interest because of their many desirable properties [1]. These are most easily synthesized by the polymerization of polar monomers. Among the polymerization procedures, transition metal-catalyzed routes are particularly attractive because of the potential ability to (a) control polymer tacticity and chirality, and (b) incorporate both polar and non-polar monomers into the polymer chains. Unfortunately, most transition metal-based olefin polymerization systems are not very tolerant of functionalities present in polar monomers, especially if the functionality is close to the C=C bond [2]. In particular, early transition metals are highly oxophilic, resulting in inhibition of polymerization by oxygen-containing functionalities in the monomer. Even with late transition metals, inhibition of polymerization due to coordination of functionalities in the monomer or in the polymer chain can and does occur. Below we cite some examples of this phenomenon.

9.2

Results and Discussion

The palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide is, by now, well documented [3]. The usual catalyst employed is a cat-

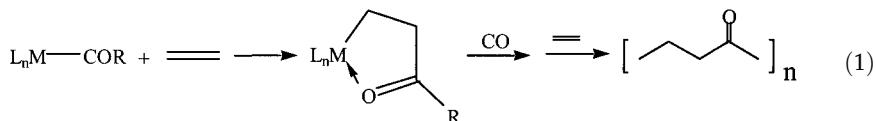
Late Transition Metal Polymerization Catalysis.

Edited by Bernhard Rieger, Lisa Saunders Baugh, Smita Kacker, Susanne Striegler

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ionic palladium(II) species incorporating a bisphosphine or a bisamine ligand. The chain growth occurs by alternate insertions of carbon monoxide and olefin into an initial Pd–C bond (Eq. (1)). We and others have examined the olefin insertion step [3 a, 4, 5].



As shown in Eq. (1), following insertion the newly formed ketone coordinates to the metal through the oxygen. This is specifically illustrated by the crystal structure of the product formed by norbornene insertion into the Pd(II)–Me bond in $\text{Pd}(\text{PPh}_3)_2(\text{MeCN})(\text{COMe})^+$ (Fig. 9.1) [3 a].

Several structural features are noteworthy. First, the *exo, exo*- stereochemistry is consistent with the expected *cis* insertion of the olefin. Second, the organic fragment formed by insertion acts as a bidentate ligand due to coordination of the acyl oxygen. However, the binding of the acyl oxygen is not very strong. This can be seen by comparing the Pd–P bond distances for the two PPh_3 ligands. The Pd–P distance of 2.236 Å for the PPh_3 *trans* to the acyl oxygen is one of the short-

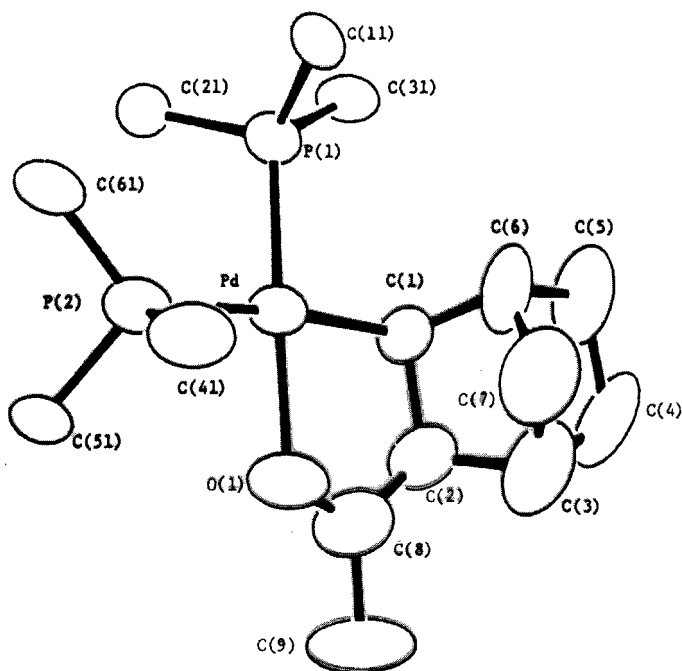
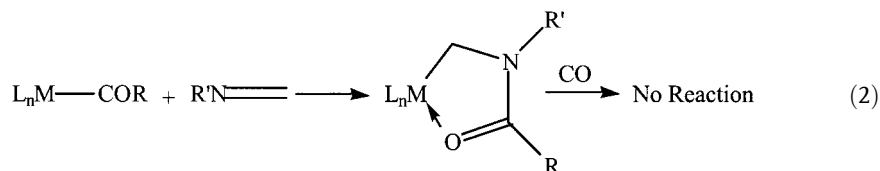


Fig. 9.1 View of the inner coordination sphere of $[\text{Pd}(\text{PPh}_3)_2(\text{C}_7\text{H}_{10}\text{COCH}_3)](\text{BF}_4)$ including the entire chelating 2-acetylnorborn-1-yl ligand.

est ever observed. In contrast, the Pd–P distance of 2.435 Å for the PPh₃ *trans* to the alkyl carbon is the longest known! Clearly, this difference reflects the very different *trans* influences of the σ -bonded alkyl and the dative-bonded acyl oxygen located *trans* to the respective PPh₃ ligands. Since the Pd–O interaction is weak, the coordinated oxygen is easily displaced by an incoming monomer, allowing the copolymerization to proceed.

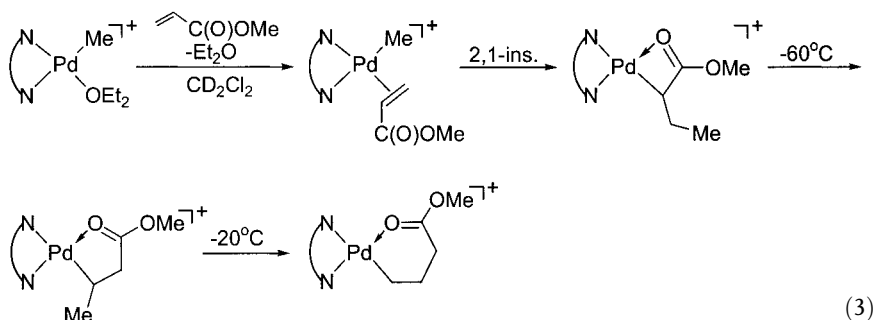
A very different situation pertains to the alternating copolymerization of imines with carbon monoxide. This reaction is of interest because, if successful, it would constitute a new general procedure for the synthesis of polypeptides. The sequence of steps leading to chain growth are similar to those observed for the alternating olefin-carbon monoxide copolymerization, with the insertion of the imine into the metal-acyl bond replacing the corresponding olefin insertion step. Indeed, imine insertion into the metal-acyl bond in cationic bisphosphine or bisamine-Pd(II) complexes does occur readily [6]. As with the insertion of olefin into metal-acyl bonds, the corresponding imine insertion results in a metal-bound amide in which the oxygen of the amide carbonyl group is coordinated to the metal (Eq. (2)).



Unlike the situation in olefin-carbon monoxide copolymerization, however, the Pd–O interaction is fairly strong and cannot be disrupted by an incoming monomer (carbon monoxide) and further chain growth ceases. The difference lies in the greater negative charge and, therefore, stronger coordinating ability of the carbonyl oxygen of an amide fragment. Interestingly, the insertion of carbon monoxide apparently occurs readily in analogous neutral species where the amide carbonyl is not coordinated to the metal [7]. It is also interesting to note that while imine insertion into Pd(II)–acyl bonds is observed, the corresponding insertion into Pd(II)–alkyl bonds does not occur [6]. Almost certainly, the formation of the very strong amide linkage constitutes the added driving force in the former reaction [8].

A similar inhibition, but not cessation, of polymerization was observed by Brookhart in his work on the copolymerization of ethylene with methyl acrylate that is catalyzed by cationic bisimine-Pd(II) complexes [9]. Here again, the coordination of the oxygen atom of the ester group of acrylate significantly slows down polymerization and leads to lower molecular weight materials (Eq. (3)).

A final illustration of the effect of coordinating functionalities on the polymerization of olefins by cationic metal complexes involves norbornene derivatives. The species, [Pd(PR₃)(Me)]⁺, generated *in situ* by halide abstraction from [Pd(PR₃)(Me)(Cl)]₂, is an extremely active catalyst for the insertion polymerization of norbornene with a rate exceeding of 1000 tons norbornene/mol Pd · hour at


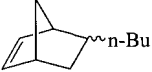
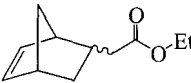
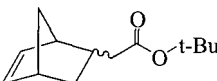


25 °C [10]! However, the polymerization rate was found to decrease dramatically for norbornene derivatives with pendant oxygen functionalities on the side opposite to the C=C bond (Tab. 9.1) [10].

Based on the ¹³C-NMR shifts, one can surmise that the electronic effect of the substituent on the C=C bond is minimal. Thus, the vinyl carbons of the norbornene resonate at 135.5 ppm, while those of 5-norbornene-2-carboxylic acid ethyl ester appear at 137.7 and 132.5 ppm (*endo*) and 138.1 and 135.9 ppm (*exo*).

Because they are synthesized by Diels-Alder reaction, functionalized norbornene derivatives sold commercially consist of *exo* and *endo* isomers with the latter predominating. The drop in polymerization rate for functionalized norbornene derivatives may be ascribed to the formation of a chelate by coordination of the metal to the functionality and the C=C bond along the *endo* face (see Fig. 9.2).

Tab. 9.1 Polymerization results with palladium(II) complex [10].

Monomer	"Pd(PPh ₃) (CH ₃)" [mol]	Monomer [mol]	Reaction time	Temp. [°C]	Yield [%]	M _w ^{a)}
	3.02 × 10 ⁻⁷	0.106	< 2 min	25	~ 100	Insoluble
	7.56 × 10 ⁻⁵	0.053	~ 2 min	25	~ 100	212900
	2.94 × 10 ⁻⁵	0.012	24 h	60	40	6500
	2.94 × 10 ⁻⁵	0.010	24 h	60	38	6400

a) Obtained relative to polystyrene standards in CHCl₃.

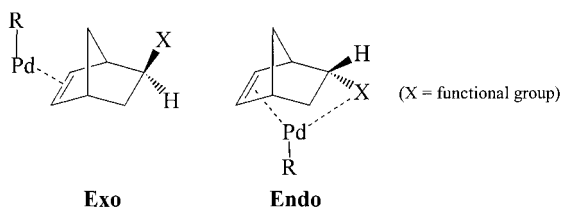


Fig. 9.2 Modes of bonding for functionalized norbornene derivatives.

This has two detrimental effects on polymerization. First, chelation strengthens the metal-olefin interaction, thereby raising the barrier for the insertion step. Second, it forces insertion through the *endo* face, in sharp contrast to the known propensity for norbornene to insert into metal-carbon bonds through the less hindered *exo* face [3 a, 5]. Consistent with this hypothesis has been our observation of the preferential uptake of the *exo* isomer in the polymerization of functional norbornene derivatives by $[\text{Pd}(\text{PR}_3)(\text{Me})]^+$. For example, Fig. 9.3 shows the uptake profile versus time for the polymerization of 5-norbornene-2-carboxylic acid ethyl ester starting with a monomer isomer ratio of 22% *exo* to 78% *endo*. Indeed, under certain conditions a polymer can be obtained from the *exo* isomer but not the *endo* isomer [10].

Given the published studies that indicate that the insertion of nonfunctionalized norbornenes into metal-carbon bonds occurs with *exo, exo*- stereochemistry (e.g., Fig. 9.1) we sought to determine whether the presence of an *endo* functionality would change the insertion stereochemistry. Because of the relative instability of the catalytically active palladium species, detailed studies encompassing the coordination and insertion of norbornene derivatives were carried using the model

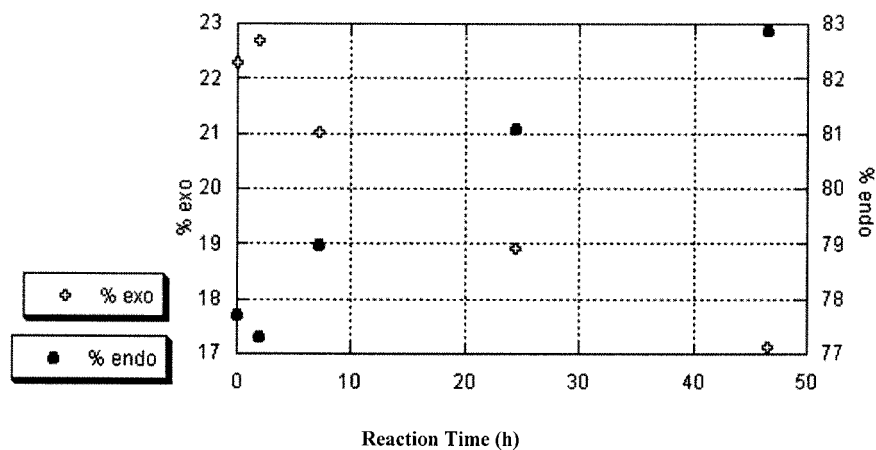
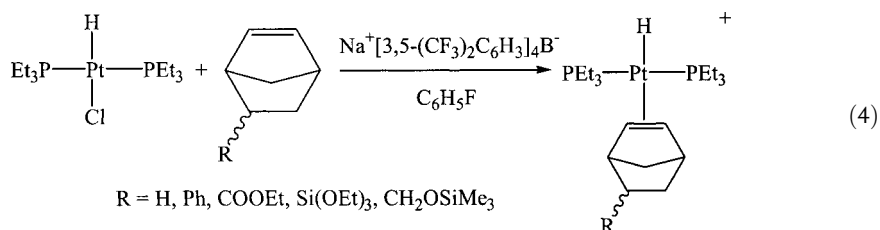


Fig. 9.3 Plot of unreacted monomer versus time for the polymerization of 5-norbornene-2-carboxylic acid ethyl ester.

$[(\text{Et}_3\text{P})_2\text{Pt}(\text{H})]^+$ fragment. This species was produced *in situ* via chloride ion abstraction from $\text{trans}[(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\text{Cl})]$ with $\text{Na}^+[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4\text{B}^-$ in fluorobenzene. When reacted with $\text{trans}[(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\text{Cl})]$ and 1 equiv. of $\text{Na}^+[3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3]_4\text{B}^-$, substituted norbornenes formed $\text{trans}[(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\eta^2\text{-norbornene-R})]^+$ instantaneously and quantitatively (Eq. (4)). Heating the NB-COOEt adduct of $(\text{Et}_3\text{P})_2\text{PtH}^+$ in fluorobenzene the presence of 5 equiv. of NB-COOEt led to the formation of the product derived by the insertion of norbornene into the Pt(II)–H bond.



The crystal structure of the insertion product is shown in Fig. 9.4 [10]. It is clear that the insertion has occurred from the *endo* face of the norbornene substrate. As with the structure shown in Fig. 9.1, the two Pt–P bond distances are substantially different from one another. The Pt–P distance *trans* to the Pt–carbon bond is significantly longer (2.355 versus 2.211 Å).

Thus far, we have confined our discussions as to the effect of coordinating functionalities on metal-catalyzed polymerizations. Interestingly, vinyl halides, which

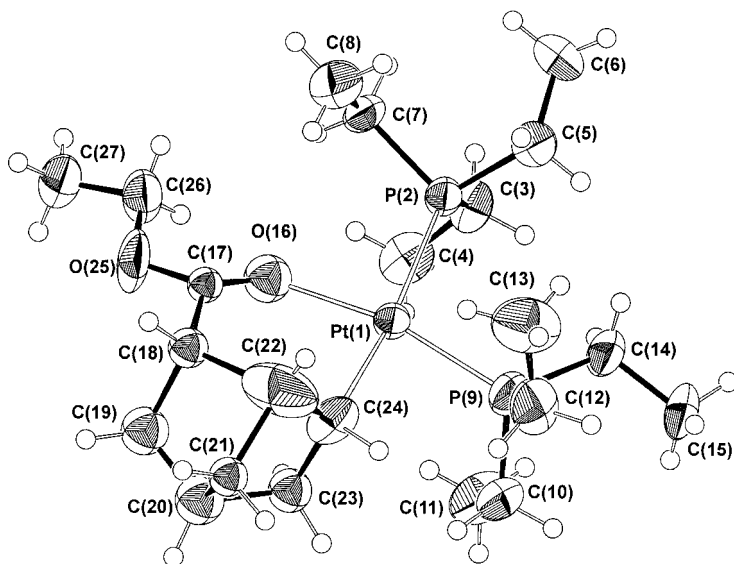
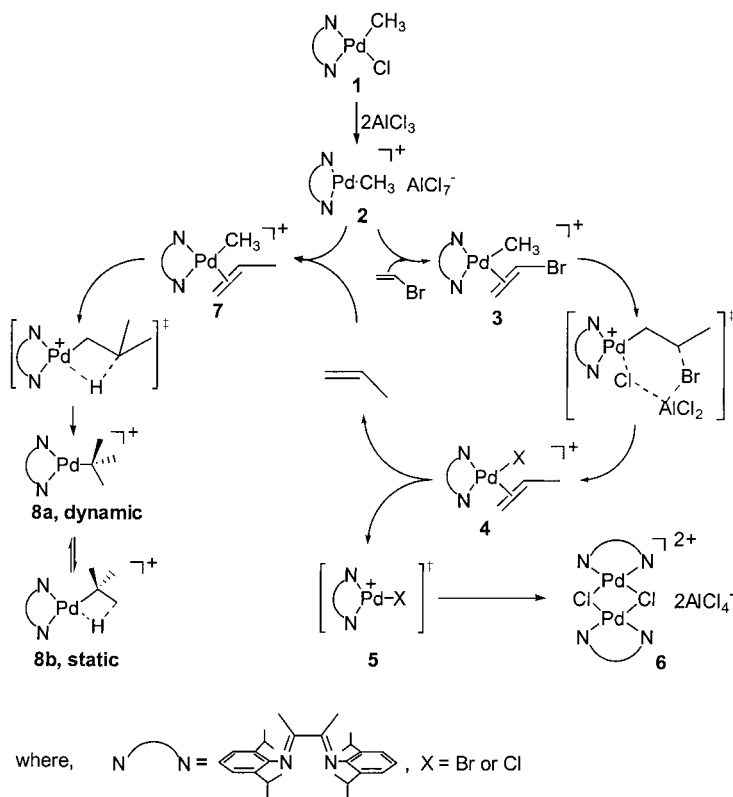


Fig. 9.4 ORTEP representation of *cis*-Pt(η^2 -C,O-(*endo,endo*)-norbornene-COOCH₂CH₃)(P(CH₂CH₃)₃)₂.

do not possess any strongly coordinating functionality, are also not polymerized by any known transition metal-catalyzed systems. Recently, Jordan [11] and Wolczanski [12] have reported the reaction of vinyl halides *rac*-(EBI)ZrMe and (*t*Bu₃SiO)₃TaH₂, respectively. It was demonstrated that, following 1,2-insertion of the alkene, β -halide elimination occurs to generate a metal-halide bond. Since the halophilicity of the transition metal ions tends to decrease on going from left to right in the periodic table, we have examined the reactivity of vinyl halides towards a late transition metal complex (palladium) [13].

The starting point of our investigation was the Brookhart-type cationic Pd(II)-methyl species, **2** generated in our case by the addition of two equivalents of AlCl₃ to the corresponding neutral Pd(II)-methylchloride, **1** (Scheme 9.1) [13]. Several equivalents of vinyl bromide were added to a CD₂Cl₂ solution of **2** at -90°C and the reaction mixture was monitored by ¹H NMR spectroscopy as it was gradually warmed up (Scheme 9.1).

The coordination of vinyl bromide to the metal center in **2** was observed even at -86°C , resulting in the formation of **3**. Warming the reaction mixture to -74°C



Scheme 9.1

resulted in the formation of the propene-coordinated species, **4**, suggesting 1,2-alkene insertion followed by β -bromo elimination. Propene is gradually lost from **4** and is trapped by unreacted **2** to form **7**. The cationic Pd(II)-halide species arising from **4** by propene loss converts into the chloro-bridged dimer **6** (via **5**). The structure of **6** as a dicationic complex with two aluminum tetrachloride counter-anions was established by an X-ray crystal structure determination. The identity of the halide ligand in **4** has not been established but the formation of **6** opens up the possibility of an aluminum-assisted β -bromo abstraction pathway shown in Scheme 9.1. Once formed, **7** undergoes 1,2-insertion of propene to form the known β -agostic Pd(II)-*tert*-butyl compound **8** [14].

The migratory insertion rates of bound vinyl bromide and propene in **3** and **7**, respectively, were directly measured by monitoring the disappearance of the corresponding Pd-CH₃ resonance. For propene our value was in close agreement with that reported by Brookhart [15]. For vinyl bromide, an Arrhenius plot was constructed from rate measurements done between -74 and -37°C . Our values together with those of Brookhart [9, 15] are reported in Tab. 9.2.

A Hammett plot of the relative insertion rates of substituted alkenes versus σ_p [20] yielded a straight line with a *positive* ρ (+3.41) (Fig. 9.5).

Of note is that the line encompasses values obtained by both Brookhart [9, 15] and us. Theoretical calculations have also led to a lower insertion barrier for acrylate compared to ethene [16]. This can be contrasted with a *negative* value of ρ obtained by Bercaw for alkene insertion in Cp*₂NbH(alkene) [17a]. Additionally, the second-order rate constants obtained by Wolczanski for alkene insertion into the Ta(V)-H bond follow the trend H ~ OR >> halide (F, Cl, Br) [12]. The decrease in the rate of insertion with increasing electron withdrawing effect of the substituent on the alkene in the case of early transition metal compounds has been attributed to the development of a positive charge on the carbon bearing the substituent either during alkene coordination or the subsequent insertion step [12, 17]. In Wolczanski's case, it is not been possible to separate the effect of the substituent on binding versus insertion, and the trend for the actual insertion step remains an open question. We ascribe the increase in insertion rate for the palladium-methyl complex to a ground-state effect. An alkene with an electron-withdrawing substituent coordinates less strongly to the electrophilic metal (i.e. σ -donation is more important than π -back-donation) [18]. Thus, a weaker metal-alkene bond has to be broken for the insertion to proceed (i.e., the destabilization of the alkene

Tab. 9.2 Kinetic data for insertion of alkenes into palladium(II)-methyl bond^{a)}.

Alkene	$10^3 k [\text{s}^{-1}]$	$(\Delta H^\ddagger [\text{kcal mol}^{-1}])$	$(\Delta S^\ddagger [\text{cal K}^{-1} \text{mol}^{-1}])$
Propene	0.54		
Ethene [15]	1.9	14.2 ± 0.1	-11.2 ± 0.8
Vinyl bromide	22.0	11.9 ± 0.1	-16.8 ± 0.1
Methyl acrylate [9]	55.0	12.1 ± 1.4	-14.1 ± 7.0

a) Measured or extrapolated to 236.5 K.

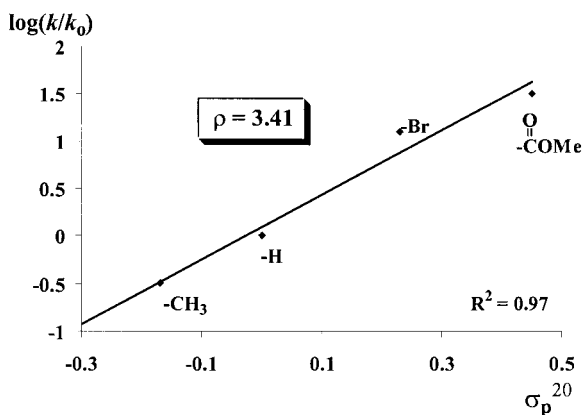
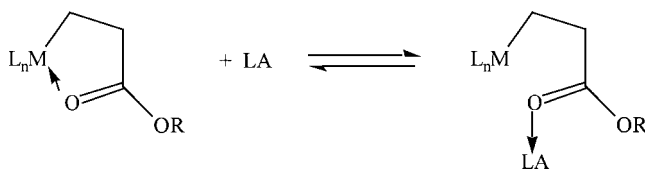


Fig. 9.5 Hammett plot for migratory insertion of alkenes into palladium(II)-methyl bond.

complex leads to a lower insertion barrier). Another surprising observation is that the observed correlation extends to propene. The slower insertion and polymerization rates of propene, when compared to ethene, are usually attributed to the steric bulk of the methyl group of the former [15, 19]. Our results suggest that, at least for the late transition metal compounds, it is the donating ability of the methyl group, rather than its size, which results in slower rate for propene insertion and, hence, polymerization. This argument applies even for the sterically encumbered Brookhart-type system. Likewise, for acrylates, the precoordination of the ester group appears to have little effect on its migratory insertion rate.

What is the implication of our work with respect to the metal-catalyzed polymerization of polar vinyl monomers? First, for the late metal compounds, the polar vinyl monomers can clearly outcompete ethene and simple 1-alkenes with respect to insertion. However, the ground-state destabilization of the alkene complex that favors the migratory insertion of the polar vinyl monomers is a two-edged sword because it biases the alkene coordination towards ethene and 1-alkenes. Indeed, we have observed the near quantitative displacement of vinyl bromide by propene to form **7** from **3** (Scheme 9.1). Thus, the extent of incorporation of the polar vinyl monomer in the polymer will depend on the opposing trends in alkene coordination and migratory insertion. The above discussion does not take into account the problem of functional group coordination for acrylates or β -halide abstraction for vinyl halides.

There are several possible approaches to circumventing functional group coordination. One obvious route is to decrease the electrophilicity of the metal center, e.g. by moving from cationic to neutral complexes. In recent theory paper [16], Ziegler has shown that the interaction of the ester group of acrylate with the metal center is weaker in neutral complexes when compared with the corresponding cationic species. On the other hand, the bonding of the olefinic functionality is not significantly affected because the weaker alkene to metal charge transfer in



(LA = Lewis Acid)

Fig. 9.6 Binding of functionality to a second Lewis acid.

the neutral complex is compensated by stronger metal to alkene backbonding. Grubbs has recently reported a neutral nickel-based polymerization system [21]. However, this system is ineffective for acrylates, presumably because the coordination of the ester group is stronger with nickel(II) than palladium(II).

Decreasing the electrophilicity of the metal center would also be expected to diminish the rate of β -halide abstraction, the “chain termination” step in the possible polymerization of vinyl halides.

Another approach to circumventing functional group coordination is to add a (second) Lewis acid that can bind to the functionality thereby preventing its coordination to the metal center responsible for polymerization. In essence there will be competition between two different Lewis acids for the same functionality (Fig. 9.6). On entropic grounds, the chelation to the polymerizing metal center will be favored. In order to overcome this, the second Lewis acid should form a stronger bond to the functionality.

9.3

Conclusion

The coordination of the functionalities that may be present either in the monomer or in the growing polymer chain to the metal center is a key impediment in the development of new transition metal-based catalysts for the insertion polymerization of polar monomers. On the other hand, rapid β -halide abstraction has prevented metal-catalyzed polymerization of vinyl halides.

9.4

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Subject Index

a

- acenaphthenechinone backbone 65 ff.
- acetylene 168
- acetylene polymerization 18 ff.
- acrylate 159, 296
 - dimerization with “naked” Ni and Pd catalysts 107
- activation
 - unsaturated substrates 5
- activity-structure relationships for olefin polymerization catalysts 61
- acyclic diene metathesis polymerization *see* ADMET
- acyl complex, of Pd
 - imine insertion 309
 - norbornene insertion 308
- adhesion
 - of Avatrel dielectric polymers 140
- adhesives 234
- ADMET
 - applications 202
 - experimental considerations for 224
 - bulk polymerization 224
 - in solid state 226
 - under vacuum 224
 - volatile monomers 225
 - with carrier gas 224
 - with solid monomers 225
 - formation of cyclics 197, 225
 - functional group tolerance in 197
 - hydrogenation of products in 202
 - kinetic 196
 - mechanism 199
 - monomer purity in 196
 - negative neighboring group effect 197
 - regiochemical and stereochemical considerations 201, 221
 - step-growth nature of 195 ff.
 - temperature dependence of rate in 222
 - tolerance of functionality 210
 - vinyl addition side reactions in 203
 - with classical metathesis catalysts 203
 - with molybdenum catalysts 204
 - with ruthenium catalysts 207, 210, 214 ff., 218, 221, 223
 - catalyst decomposition 223
 - mechanism 214 ff., 218
 - stereochemistry 221
 - with tungsten catalysts 204
- alkoxide-exchange 163
- 2-alkoxyimines 79
- alkyl exchange between iron and aluminum 89
- alkylidene proton exchange 175
- alkylidenes 199
- alkyl tin reagents in metathesis 203
- alkyne polymerization 155
- 1-alkynes 168
- allenes 300
 - arylallenes 300
- allylbenzenes 296
- (η^3 -allyl)Pd(hexafluoroacetylacetonate) 112
- alternating copolymerization 27
- amino acid-containing polymers 203, 214
- N-amino azoles 71
- N-amino-N-heterocycles 63
- Andersen, A. W. 102
- anionic chelating ligands 79
- APELTM cyclic olefin copolymers 101, 144
- AppearTM optical polymers 139, 141
- aqueous systems 237, 262
- Arduengo, A. J. III 211
- Arndt, M. 121
- aromatic atropisomeric ligands 294
- arsenic ylides 2
- N-aryl-1,2-diimine Ni precatalysts 62
 - amino-pyrroles 62
 - carbazoles 62

- indoles 62
- arylimido 166
- aryloxy(chloro)tungsten alkylidene complex 158
- asymmetric diimine ligands 41
- atactic copolymer 295
- atactic materials 290
- atom transfer radical polymerization (ATRP) 61, 235, 259f., 262, 265, 270
- aqueous 263
- emulsion polymerization 265
- AvatrelTM dielectric polymers 139f.
- N-azolyl 84
- N-azolyl 2,6-bis(imino)pyridyl metal complexes 71

b

- back-biting metathesis 197
- Baeyer-Villiger oxidation 301
- benzaldehyde as polymer endcapping reagent 205f.
- benzyl-Grignard reagents 8
- bidentate ligands 239
- bidentate Schiff-base ligands 176
- bifunctional bimetallic catalyst 14
- bifunctionally produced polyethylene 15
- binaphos system 292
- binuclear molybdenum alkylidenes 164
- BiPE *see* bifunctionally produced polyethylene
- bis(cyclopentadienyl)nickel 106
- 1,2-bis(diphenylphosphino)ethane 47
- 2,3-bis(2,6-dibromophenyl)imine butane 68, 87
- α,ω -bis(dicyclohexylphosphino)octane 176
- α,ω -bis(dicyclohexylphosphino)pentane 176
- bis(imino)pyridyl ligands 71ff.
- bis(phosphine) ligands 47ff.
 - complexation 47f.
 - ethene bridged 47f.
 - sterically demanding 47, 54
 - synthesis 47f.
- bis(phosphino) complexes 47ff., 52
 - active species 52
 - amount of substitutions 51
 - bond angles 50f.
 - bond length 50f.
 - ¹³C-NMR 52
 - conformational rigidity of the ligand spheres 54
 - ethene oligomerizations 53
 - ethene polymerization 52
 - ¹H-COSY 52
 - ¹H-NMR 52
 - influence of substitution 52
 - NMR studies 52
 - ORTEP-plot 49
 - Pd-P bond lengths 51
 - single crystal X-ray diffraction 48
- 2,2-bis(trifluoromethyl)norbornene 182
- bis(trifluoromethyl)norbornadiene 165
- bis(triphenylphosphine)
 - phenyl(chloro)nickel 76
- bis(ylide)nickel catalysts 6ff., 10, 16f.
 - acetylene polymerization 18ff.
 - activity 10
 - butadiene polymerization 17
 - cycloolefin polymerization 16
 - ethene polymerization 10
 - ligand effects 14
 - linear macromolecules 13
 - oligomers 13
 - polar group tolerance 17
 - polar monomer polymerization 17
 - polyethylene properties 12
 - polynorbornenes 16
 - self-branching effect 14
 - X-ray structure 9
- bis-dihydrooxazole ligands 292
- bisphosphine monooxide 286
- block copolymers 252
- branched macromolecules 13ff., 86
 - long chain 14
 - short chain 13
- Bridgestone nickel catalyst system 125
- Bridgestone Tire Company 125
- Brookhart catalysts *see* Pd diimine complexes and Ni diimine complexes
- bulk polymerization with nickel ylide catalysts 17
- butadiene 259
 - monomer 237
 - polymerization 17
 - polymerization with “naked” Ni and Pd catalysts 107
 - polymerization with Ni(C₁₂H₁₈) 126
 - trimerization 125
- butyl methacrylate 264
- butylnorbornene 137, 147
- 4-*tert*-butylstyrene 290

c

- Canale 237
- caprolactone 128
- N-carbazolyl 84
- carbenes 199, 255
- σ -carbon ligands 3

- carbon monoxide 239
 - alternating copolymerization with olefins 279, 307 ff.
 - olefin insertion step 308
 - *trans* effects in 309
- carbonylation of ethene 287
- Carilon 279
 - end groups of the polymers 280
 - mechanism of polymerization 280
- Carothers equation 196
- catalyst
 - aluminoxanes 16
 - bidentate ligands 244
 - chromium(II) 14
 - copper-based 263 f.
 - Cr(II)/silica 15
 - diffusion 265
 - efficiency 269
 - heterogeneous 15
 - hydrophobic 246, 265
 - iridium 256
 - lipophilic 244, 257
 - molybdenum 250
 - nickel 12 ff., 16, 244
 - palladium 16, 240
 - Phillips 231, 235, 243
 - P-O-substituted 245
 - rhodium 235, 256
 - ruthenium 250, 264
 - salicylaldimine-based 245
 - stability 246, 256
 - towards water 251
 - titanium 15
 - tungsten 250
 - water-insoluble 244
 - water-soluble 257, 268
 - Ziegler 231, 235, 243
- cationic palladium catalysts
 - for norbornene/ethene copolymerization 147
- C-H activation 21
- chain
 - active 260
 - dormant 260, 263
 - growth 14, 241, 244 ff.
 - polyacetylene 23
 - polyethylene 15
 - propagation 11, 17
 - rotation 54
 - termination 11, 14, 268
 - with vinyl halides 316
 - transfer 11, 245
 - in ADMET 200
 - walking 14, 86, 94
- Chauvin mechanism for metathesis 194
- chelate ligand Ph₂PCHCPhO 8
- chelating diphosphines 283 ff.
 - C₄-bridged 285
 - dppp-like ligands 285
 - hemilabile dppp 285
- chiral alkoxide 166 f.
- chiral binaphtholate ligands 162
- chiral complexes 31, 38
- chiral conformations of ligands 35, 38
- chiroptical properties 294
- chromium bis(acetylacetonate) 106
- chromium carbenes 157
- chromophores 23
- coatings 234
- cobalt(II)-bisimino(pyridine) complexes 39
- co-catalysts
 - aluminium 17
- colloid chemistry 254
- combinatorial methods 61
- complex
 - carbene 252 f.
 - nickel(II) 246
 - rhodium 243, 257
 - titanium 255
- control of copolymer linearity 55
- control of polymer linearity 43
- control of polymer microstructure 55
- copolymerization 259, 269
 - aqueous 242
 - copolymers of styrene 288
 - ethene-CO 29
 - ethene/propene 13
 - ethene-styrene 15
 - ethene 247
 - ethene/CO 239, 242
 - of 1,1-dimethylallene 300
 - of internal olefins 297
 - olefin-CO 239
 - with carbon monoxide
 - 1-olefins 288
 - regiochemistry of the copolymers 288
 - stereochemistry of the produced copolymers 289
- copolymers
 - amphiphilic 270
 - ethene-CO 240
 - of norbornene 286
 - 1-olefin-CO 241
 - propylene-CO 239
- Cp*RuClL 212
- cross metathesis (CM) 195

- [[η^3 -crotyl](cycloocta-1,5-diene)nickel]
 - hexafluorophosphate *see* "naked" nickel catalysts
 - [[η^3 -crotyl](cycloocta-1,5-diene)palladium]
 - hexafluorophosphate *see* "naked" palladium catalysts
 - [[η^3 -crotyl]Ni(μ -Br)]₂ 109
 - [[η^3 -crotyl]Pd(μ -Cl)]₂ 109
 - crystalline polyethene 42
 - C_{2v}-symmetric catalytic systems 294
 - C₁-symmetric ferrocenylphosphines 296
 - C_s-symmetric ligand 294
 - cyclic alkynes 169
 - cyclic diene metathesis 169
 - cyclic olefins 163, 171, 173
 - addition polymerization 16, 104
 - norbornene 16
 - cyclic oligomers 197, 225
 - cyclic strained olefins 159
 - cycloaddition 200
 - cyclobutenes 104
 - cyclodextrins 266
 - cyclo-1,5-octadiene 109 f., 161, 182, 197, 210, 254
 - (cyclooctadiene)palladium methyl chloride 147
 - cyclooctatetraenes 168
 - cyclooctene 254
 - cyclopentene 254, 297
 - addition polymerization 104
 - cyclopropenes 104
 - cyclotrimerization 256
 - Cymetech 103
- d**
- DCPD *see* dicyclopentadiene
 - 1,9-decadiene 196, 198, 203, 210, 214, 216, 220, 222, 226
 - 1-decene 115, 127
 - 5-decylnorbornene 109, 125, 127
 - degree of branching 30
 - desymmetrized catalysts 40
 - dextran standards 252
 - diastereomeric ligands 295
 - 2,6-dibromophenyl substituents 67
 - dicationic ruthenium vinylidene 181
 - 2,6-dichlorophenyl substituents 88
 - dicyclopentadiene 103, 105, 159, 238
 - copolymers 298
 - α,ω -dienes 164, 299
 - 2,3-dihydrofuran 157
 - diimine complexes 30 ff.
 - complex synthesis 32
 - 2,6-diaryl-substituted 31
 - modified 31
 - solid state structures 33
 - diimine ligand 32
 - role in ethene/norbornene copolymerization with cationic palladium catalysts 148
 - 1,4-diketones 62
 - (dimethoxyethane)Ni(3,5-(CF₃)₂C₆H₃)₂ 138
 - di(methylcyclopentadiene) 298
 - dinitrogen ligand 283, 285
 - 2,2-diphenylcyclopropene 161, 171
 - 2,6-diphenyl-modified aniline moieties 40
 - 1,1-diphenylprop-2-ynol 180
 - 2,6-diphenyl-substituted anilines 32
 - diphosphines 176, 239
 - 1,1'-diphosphinoferrocene 176
 - dipropargylmalonate 168 f., 172
 - dispersions
 - aqueous 234
 - divinylbenzene 15, 164
 - 2,10-dodecadiene 220
 - donor ligands 28
 - DPPE *see* 1,2-bis(diphenylphosphino)ethane
 - DPPE-PdCl₂ 49
 - dppp 239
 - droplet 245, 248, 265
 - Durhan route 168
 - DuvcorTM photoresist polymers 139, 142
- e**
- elastomers 103, 105
 - electron-poor strained olefins 299
 - electrophilic palladium(II) center 52
 - elimination
 - β -hydride 255
 - emulsifier 241
 - emulsion 249
 - aqueous 244
 - polymerization 183
 - enantiomorphic site 294
 - enantiosite control 297
 - encapsulation 44
 - endcapping in metathesis polymerization 205
 - endgroups, polymer 241
 - determination 13
 - EPDM *see* ethene propene diene monomer technology
 - ethene 5, 245
 - as byproduct in ADMET 196, 199
 - as chain transfer agents in insertion polymerization of norbornene 115, 123

- copolymerization with norbornene 145, 147
- copolymer with propene 203
- via ADMET 203
- oligo-/polymerization 10
- polymerization 10ff.
- nickel catalysts 10
- molecular weight 11
- reaction with Pd diimine complexes 314
- ethene homopolymers 27ff.
- high linearity 39
- molecular weight of 39
- ultrahigh molecular weight 39
- ethene monomer 43
- ethene oligomerizations 28, 43ff.
- bis(phosphino) complexes 53
- isomeric mixture of olefins 46
- N \cap N ligands 46
- P \cap N ligands 46
- P \cap P ligands 46
- ethene oligomers
- ^{13}C -NMR spectrum 54
- DSC measurements 53
- GC/MS measurements 53
- ^1H -NMR measurements 54
- IR spectrum bands 54
- ethene polymerization 37ff., 52
- addition of hydrogen 39
- bis(phosphino) complexes 52
- control of polymer linearity 43
- degree of branching 43
- β -hydride elimination 43
- 2,1-insertion 43
- Pd-P bond lengths 51
- ethylene *see* ethene
- ethylidene norbornene (ENB) 105
- ethyl vinyl ether 128, 211

f

- Fischer carbene 204, 209
- Flory distribution 198
- fluorinated alkoxides 169
- functional groups 163
- functional group-tolerant ruthenium systems 170
- functional monomers *see* polar monomers
- functional polyolefins 307
- via ADMET 202
- functionalized olefins 296
- future fields of interest for transition metal catalysts 55

g

- Georgia Institute of Technology Packaging Research Center 140
- glass transition temperature 241
- importance for processing of cycloaliphatic polymers 103, 106, 115, 123
- glycopolymers 250
- Goodrich, B.F. 103, 140f.
- Grubbs catalysts *see also* $\text{RuCl}_2(\text{PR}_3)_2\text{CHR}_1$, $\text{RuCl}_2(\text{NHC})(\text{PR}_3)\text{CHR}$, and ruthenium metathesis catalysts 29, 171, 209
- mechanism of ADMET with 14

h

- β -halide abstraction 315
- HDPEs *see* high density polyethylenes
- Heck coupling 266
- 1,6-heptadiene-4-ol 299
- Hercules 103
- heteroatom-containing Ru-carbenes 181
- N-heterocyclic carbene
- ADMET 179
- cross-metathesis 179
- dihydro analogues 178
- imidazoline-2-ylidenes 177
- in ring closing metathesis 179
- in ruthenium-based ROMP 177
- other imidazole ligands 179
- N-heterocyclic carbene (NHC) ligands and complexes 211
- role in metathesis polymerization 217
- synthesis 13
- heteroditopic ligands 286
- heterogeneous micellar nucleation 232
- hexadecylnorbornene 125
- 1,5-hexadiene 198, 203, 210, 299
- hexafluoroantimonic acid 126
- high density polyethylenes 12
- highly branched polyethylene 87
- high molecular weight polymers 28
- Hoechst 101, 144
- homogeneous catalyst
- ylide nickel complexes 6
- homogeneous nucleation 232
- hybrid P-N ligands 293
- hybrid terdentate carbene ligand complexes 298
- β -hydride abstraction 38
- β -hydride elimination 14f., 39, 86
- hydridotris(pyrazolyl)borate 177
- hydroethynylation 255
- hydrophobicity 265

hydroxyimine ligands 80
2-hydroxyimine nickel system 91

i

Idemitsu Kosan 105
imines, alternating copolymerization with
olefins 307
– imine insertion step 309
imino-phosphine complexes 298
N-indolyl 84
trans influence 45
insertion 243, 249
– ethene 14f.
– styrene 15, 292
1,2-insertion of styrene 15
in situ generation of ruthenium alkylidenes 174
in situ reactions 41
intact ylide ligand 7
intermediate
– metal alkyl 254
– metal carbene 254
ionization potential 4
iron(II)-bisimino(pyridine) complexes 39
isomerization of olefins 207
isotactic copolymer 291, 295
isotactic styrene copolymers 291

j

josphos 296

k

ketophosphine 286

l

late transition metal catalysts 28ff., 55
latex 65, 231, 244, 246f., 249, 254, 258, 270
– electrostatic repulsion 231
– properties 269
LCB-PE *see* long chain-branched polyethylene
LCDs *see* liquid crystal displays
ligands 5
– bidentate P-O- 245
– phosphanes 5
linear α -olefins 28
linear low density polyethylene (LLDPE) 13
linear macromolecules 13, 54
linear polyethylene 40
linkages, polymer backbone
– carbonyl 267
liquid crystal displays 22
living isotactic copolymerization 291
living polymer 163

living polymerization of 2-butyne 156
living systems of ROMP 174
LLDPE *see* linear low density polyethylene 13
long chain-branched macromolecules 14
long chain-branched polyethylene 14
low molecular weight polyketones 287, 292
low temperature impact modifiers 68

m

macromolecules 13ff.
– branched 13f.
– linear 13
– long chain-branched 14
– short chain-branched 13
– unsaturated end groups 13
manganese bis(acetylacetonate) 106
materials, properties of 23
– color 24
– nonlinear optical devices 23
materials, polymeric
– branched 243
– linear 244
– Tailor-made 13
MATPAC *see* matrix polyacetylenes
matrix polyacetylenes 18
– homogeneous types 19
matrix polymer backbone 21
3MCompany 141
MDPE *see* medium density polyethylene
mechanism
– catalytic 15
– insertion 238
medium density polyethylene 13
methyl-Duphos-modified catalyst 297
melt-processing 103
(2-Me)₂P \cap P(2-Me)₂ ligand 46
metal carbene 155
metal-carbon bond 3, 260
– monodentate σ -complex 4
– polyhapto π -ligands 4
– π -systems 4
metallacycle 9, 156
metallacyclobutanes 159, 200
metallocenes 15
metathesis 254, 256
– applications in materials 183
– catalysts
– – classical 203
– polymerization 155
– based reactions
– – dissociative mechanism 172

- effect of phosphine size 172
 - rate of catalysis 172
 - trans*-metathesis 198, 200 ff., 206, 221
 - methacrylic acid 262
 - methyl acrylate 314
 - methylene phosphorane 81
 - methylenecyclopropane 298
 - methylidenes 173, 199
 - 1-methylnorbornene 158
 - methyltrioxorhenium 170
 - Metton® 103
 - micelle 232, 246, 253
 - microelectronics 139
 - microemulsion 249
 - microstructure 16, 27
 - control 27
 - migratory insertion 14, 254
 - miniemulsion 241, 246 f., 254
 - technique 265
 - Mitsui Petrochemicals 101, 144
 - molecular weight 39
 - distributions 264
 - nickel ylide catalysts 11
 - of polyethylene 11
 - with high 17
 - with ultrahigh 17
 - molybdenum alkylidenes 162
 - molybdenum bisimidodichlorides 162
 - molybdenum bisimidodialkyl complexes 162
 - molybdenum metathesis catalysts 103, 204
 - tolerance of functionality 206
 - molybdenum(imidoalkylidene) bistri-
flates 162
 - molybdenum-methylidenes 173
 - monoclinic crystals 49
 - monomers
 - acrylic 17
 - butadiene 237
 - olefinic 236
 - water-insoluble 264
 - water-soluble 261, 263, 265 f.
 - monomethyl palladium complex 70
 - monophosphine adducts 172
 - multichip modules (mcms) 139
- n**
- "naked" nickel and palladium catalysts 109
 - history of 107
 - norbornene polymerization with 110, 112 f., 118, 123, 138
 - block copolymers 118
 - control of glass transition tempera-
ture 123
 - functional monomers 138
 - insertion mechanism 110
 - microstructure 112
 - propagation and chain transfer mecha-
nism with α -olefins 113 ff.
 - norbornene oligomerization with 119
 - norbornene reaction injection molding
with 108
 - synthesis of 108
 - National Institute of Standards and Technol-
ogy 141
 - natural products syntheses 194
 - neoglycopolymers 252
 - new polymer materials 55
 - Ni(C₁₂H₁₈) 125 f.
 - nickel bis(acetylacetonate) 106
 - nickel bis(cyclo-1,5-octadiene) 126
 - nickel bis(2-ethylhexanoate) 125, 128
 - nickel catalysts 1, 10 ff., 27 ff., 38
 - activity 10
 - ethene polymerization 10
 - multi-component
 - history 125
 - norbornene polymerization with 126
 - reaction with polar monomers 128
 - nickel center 9, 38
 - nickel complexes
 - dibromo complexes
 - polymerization experiments 46
 - diimine complexes 30, 37 ff., 42, 104
 - bulky substituents 40
 - catalyst activities 38 ff.
 - desymmetrized catalysts 40
 - 2,6-diphenyl-modified aniline moi-
eties 40
 - ethene polymerization 37 ff.
 - synthesis 37
 - methyl phosphorane complexes 81
 - pyridine-carboxylate ligand 29
 - salicylaldiminato ligand 30, 91
 - steric hindrance and active center 43
 - terphenyl diimine complexes 40 ff.
 - *p*-*tert*-butyl substituted ligand 41
 - *p*-methoxy substituted ligand 41
 - polymerization reactions 41
 - synthesis 40
 - nickel coordination sphere
 - trans orientation 7
 - nickel ylide catalysts 10 ff.
 - activity 10 f.
 - molecular weight of polyethylene 11

- nickel-dithiophenol 287
- nickel-phenylpyrazolylborate 287
- nickel-pyridine 287
- nickel-phenyl group
- ortho and para ^{13}C NMR signals 8
- nickel(2,2,6,6-tetramethyl-3,5-heptanedionate)₂ *see* Ni(dpm)₂
- nickel[2,4,6-tris(trifluoromethyl)phenyl]₂(1,2-dimethoxyethane) 131
- Ni(dpm)₂ 128
- [Ni-Ph(Ph₂PCHCMeO)(i-Pr₃PCH₂)]
 - X-ray structure 9
- [Ni-Ph(Ph₂PCHCMeO)(Ph₃P)]
 - X-ray photoelectron spectroscopy 8
- [Ni-Ph(Ph₂PCHCMeO)(Ph₃PCH₂)]
 - X-ray photoelectron spectroscopy 8
- [Ni-Ph(Ph₂PCHCPhO)(Me₃PCH₂)] 6 ff.
 - ^{13}C NMR 7 f.
 - ^{31}P NMR 7
- Nippon Zeon 103
- cis*-[Ni(PO)₂] bis(chelate) complexes 8
- NLO polymers 24
- N \cap N ligands 43
- nonlinear optical devices 23
- nonlinear refractive index 23
- norbornadiene 112, 159, 238, 298
- norbornene 238, 246, 249 f., 253 f., 259, 298
 - 5-alkyl derivatives 106, 108, 125, 127
 - polymerization of 106, 108, 125, 127
 - copolymerization with ethene 145, 147
 - copolymerization with α -olefins 105 ff., 113
 - functional derivatives 106, 128, 131, 137, 146, 310 f.
 - *exo* vs. *endo* bonding effects 310 f.
 - polymerization of 106, 128, 131, 137, 146, 310
 - polymer properties of 137
 - reaction with [(Et₃P)₂Pt(H)]⁺ complex 311 f.
 - imides 172
 - insertion polymerization 105 ff., 110, 112 f., 118, 123, 126, 128, 131, 135, 138, 145, 309
 - with electrophilic Pd(II) complexes 105
 - with metallocenes 105
 - with multi-component nickel catalysts 126, 128
 - – effects of oxygen donors 128
 - with “naked” Ni and Pd catalysts 107 ff., 110, 112 f., 118, 123
 - – block copolymers 118
 - – control of glass transition temperature 123
 - – insertion mechanism 110
 - – microstructure 112
 - – propagation and chain transfer mechanism with α -olefins 113 ff.
 - with [Pd(PR₃)(Me)]⁺ 309
 - with (η^6 -toluene)Ni(C₆F₅)₂ 131, 135, 138
 - – functional monomers 138
 - – mechanism 135
 - – polymer endgroup structure 131
 - with P-O chelate Ni complexes 145
 - with Ziegler systems 105
 - oligomerization 119, 132
 - oligomer NMR spectra 119 ff.
 - reaction injection molding 108
 - terpolymerizations 147
 - with Idemitsu catalysts 106
- 5-norbornene-2-carboxylic acid ethyl ester 310 f.
- 5-norbornene-2-carboxylic acid *t*-butyl ester 310
- Norsorex[®] *see* polynorbornene
- N-Pd-N plane 33
- N-pyrrolyl substituents 84
- nucleation 253, 265
 - heterogeneous micellar 232
 - homogeneous 232
- O**
- 1,7-octadiene 299
- octatetraene 164
- olefins
 - equilibration in ADMET 201 f., 221
 - metathesis 251, 255
 - polar-functionalized 269
 - polymerizations 269
 - – as chain transfer agents in insertion polymerization of norbornene 115, 127
 - copolymerization with norbornene 105, 144
 - – β -hydride elimination 14
- α -olefins 15
- oligomerization 6
- oligomerization catalyst 5
- oligomers 84, 86
- optical polymers 141
- optical signals
 - electrical signals 23
- organoboronates 266
- organomolybdenum chemistry 161
- OsCl₃ 207

osmium dineopentylbisneopentylidene 183
 7-oxanorbornadiene 166
 7-oxanorbornene 166, 207f.
 oxazoline-phosphine complexes 286
 oxidative addition 255, 268

p

Paal-Knorr condensation 62ff.
 paints 234
 palladium bis(2-ethylhexanoate) 137f.
 palladium catalysts 27ff.
 palladium center
 square-planar 33
 palladium chloride 106
 palladium(II) diimine complexes 30, 42
 – active species for polymerization 52
 – bond angles 35
 – bond lengths 35
 – bulky substituents 40
 – *tert*-butyl substituent 34
 – 2-(4-*tert*-butyl)phenyl groups 35
 – chiral conformation 35
 – C_2 -symmetric coordination geometry 34
 – desymmetrized catalysts 40
 – 2,6-diphenyl-modified aniline moieties 40
 – ethene polymerization 37ff.
 – influence of para substituents 36
 – ORTEP plot 34
 – schematic illustration 36
 – stereorigid ligand arrangement 37
 – steric hindrance and active center 43
 palladium monomethyl complexes
 – ethene polymerization 37ff.
 palladium(II) terphenyldiimine complexes 40ff.
 – *p-tert*-butyl substituted ligand 41
 – *p*-methoxy substituted ligand 41
 – polymerization reactions 41
 – synthesis 40
 palladium(2,2,6,6-tetramethyl-3,5-heptanedionate)₂ (Pd(dpm)₂) 131
 PANPAC *see* polyacrylonitrile-based polyacetylene
 parallel synthesis of ligands 61
 paramagnetic compounds 65ff.
 particles
 – core-shell 270
 (PCCONi) metallocycles 9
 [Pd(CH₃CN)₄][BF₄]₂ 105
 PdCl₂P₂ sequence
 – square planar coordination plane 50
 – tetrahedral environment 51

Pd diimine complexes
 – polymerization of cyclopentene 104
 – reaction of alkenes with 314
 – reaction of vinyl bromide with 313
 PE *see* polyethylene
 1,4-pentadiene 299
 Pentam® 103
 peptides 203
 ω -perfluoroalkyl-1-alkenes 295
 phenoxide 166f.
 phenylacetylene 257
 phosphane catalysts 8
 phosphane nickel complex 5
 – oligomerization catalyst 5
 – SHOP 5
 phosphine ligands 2, 268
 – dissociation in ADMET 215ff.
 – role in metathesis polymerization 214, 217
 – role in norbornene polymerization with nickel and palladium catalysts 136
 phosphine-dihydrooxazole 293f.
 phosphonium salt 3
 phosphorus ylides 1
 – transition metal-carbon bonds 3
 – complex 5
 phosphorus-carbon ylides 1ff.
 – basicity 2
 – heteroatom effects 2
 – HOMO 2
 – ionization potentials 1f.
 – oxidizability 2
 – proton affinity 2
 – reactivity 2
 photoresist polymers 141
 P-imines 12
 P \cap N chloromethyl palladium complexes 44f.
 – isomers 45
 P \cap N ligands 43ff.
 – characterization 44
 – palladium complexes 44
 – synthesis 44
 P \cap N palladium complexes
 – bond angles 50
 – bond length 50
 – ORTEP plot 45
 – X-ray structure 45
 P \cap NPdClMe complexes *see* P \cap N chloromethyl palladium complexes
 P-O chelate Ni complexes 28, 145
 – for ethene/norbornene polymerization 145

- polar matrix polymers 19
- polar monomers 161
 - electronic effects of substituents on reactivity 314
 - functional group coordination of 315
 - in ADMET polymerization 210
 - in copolymer models via ADMET 202
 - polymerization 17, 60, 106, 128, 137, 146, 307
 - reaction with Lewis acids 316
- polar ylides R_3PCH_2 8
- $P\equiv O$ ligand 29, 43
- polyacetylenes 1, 18 ff., 169, 254 f.
 - as broadband polarizers 23
 - as novel linear light polarizers 22, 23
 - highly conjugated π -systems 22
 - highly ordered 23
 - induced dipole moment 23
 - POLPAC[®] 23
 - sidechains 21
- polyacrylonitrile-based polyacetylene 19 ff.
 - as model of matrix materials 20
 - FT-IR spectrum 21
 - UV/vis absorbance 20 f.
- polyamides 140
 - 1,2-form 129
- poly(2,3-bicyclo[2.2.1]hept-2-ene) *see* polynorbornene
- polybutadiene 125, 198
- poly(butyl acrylate) 17
- polycondensation 267
- polycyclooctene 102, 250
- polycyclopentene 104
- polydispersities 84, 240, 260, 262
 - medium 17
 - narrow 17, 246
- polyelectrolytes 261
- polyenes
 - linear 22
- poly(ethyl acrylate) 17
- polyethylene 28 ff., 243 f., 247, 259
 - comparison of melting points and branching degrees 42
 - density 12
 - highly branched 55
 - highly linear 55
 - linear low density (LLDPE) 13
 - low-density (LDPE) 243
 - medium density (MDPE) 13
 - molecular weight 11, 29
 - properties 12
 - semicrystalline 246
 - short-chain branches 40
 - viscosity 12
 - waxes 88
- poly(ethylene oxide) 253
- polyketones 237, 239, 259, 283
 - containing functional groups 297
- polyketovinylene 299
- polymers
 - branched 270
 - carbohydrate-substituted 253
 - conducting 254
 - crystalline 248
 - crystallinity 259
 - latex 231
 - linearity 43
 - microstructures 235, 257 f.
 - monodisperse 263
 - properties 11
 - stereoregular 238
 - *cis-transoid* 257
 - viscosity 233
 - water-soluble 231, 263, 269 f.
- polymerization
 - acetylene 18, 22
 - aliphatic acetylenes 258
 - alkyne 237, 254, 256
 - aqueous 175, 231, 237, 241, 248, 258, 263 f.
 - biphasic 267
 - butadiene 17, 249
 - cobalt-catalyzed 249
 - control 261 f., 270
 - degree of 13, 267
 - diene 249
 - dispersion 234, 253
 - emulsion 231 ff., 248
 - ethene 14, 15, 18, 42, 243, 248
 - using different architectures of diimine complexes 42
 - ylide nickel-catalyzed 14
 - free-radical 231, 235
 - insertion 238
 - kinetics 233, 270
 - mechanism 264
 - methacrylic monomers 262
 - miniemulsion 234
 - olefin 235, 259
 - precipitation 266
 - ring opening 238
 - self-branching 15
 - single-phase 267
 - solution 234
 - step-growth-type 266
 - substituted norbornenes 157

- supercritical CO₂ 183
 - suspension 231, 234, 264
 - temperatures 19
 - transition metal-catalyzed 231
 - uncontrolled 265
 - vinylic 50
 - water 231
 - poly(methyl methacrylate) 17
 - polynorbornene 16, 102, 105 f., 250
 - block copolymers of 118
 - control of glass transition temperature 123
 - copolymerization with α -olefins 144
 - effects of oxygen donors on microstructure 128
 - functional derivatives 143
 - “solubility switch” role in photore-sists 143
 - microstructure 141
 - with “naked” Ni and Pd catalysts 112
 - with (η^6 -toluene)Ni(C₆F₅)₂ catalysts 136
 - NMR spectra of 113 ff., 130, 132
 - oligomer NMR spectra 119 ff., 132
 - oligomer synthesis 119, 132
 - with “naked” Ni and Pd catalysts 119
 - properties and applications 139, 141
 - dielectrics 139
 - optical polymers 141
 - photoresist polymers 141
 - reaction injection molding 108
 - polyoctenamer 198, 226
 - polyolefins 59, 259
 - chain-branched 15
 - polypeptides 309
 - polyphenylacetylene 256
 - poly *p*-phenylene 266 f.
 - hyperbranched 267
 - poly(propylene oxide) 253
 - poly-spiroketal structure 283
 - polystyrene 232, 248
 - poly(styrene-acrylonitrile)-based polyacetylenes 19 ff.
 - poly(vinyl acetate) 234
 - poly(vinyl-alcohol)-based polyacetylenes 22
 - P-oxides 12
 - P \cap P ligands 43 ff.
 - precisely branched polyolefins 202
 - propagation/termination ratios and ylide ligands 11
 - propene 239
 - electronic effects of methyl group 314
 - reaction with Pd diimine complexes 314
 - propene diene monomer technology 105
 - propylene *see* propene
 - 1-prop-2-ynol 180
 - protecting groups 63
 - PVAPACs *see* poly(vinyl-alcohol)-based polyacetylenes
 - P-ylides 12
 - (py)N \cap N(im) ligand 46
 - pyridine-dihydrooxazole 293 f.
 - pyridineimine complexes 290
 - pyrimidine ligand 290
 - pyrimidine-imidazoline ligand 290
- q**
- quadricyclanes 163
- r**
- radical termination 266
 - reaction injection molding (RIM) 103, 179
 - of norbornenes 108
 - rearranged ylide ligand 8 f.
 - regioirregular styrene copolymers 293
 - regioregular copolymerization 27
 - regioselectivity 294, 296
 - of ROMP 173
 - 1,2-reinsertion 14
 - 2,1-reinsertion 38
 - ring closing metathesis (RCM) 194, 197
 - mechanism 172
 - of dicyclopentadiene 181
 - transition state 172
 - ring-opening metathesis (ROM) 194
 - ring-opening metathesis polymerization *see* ROMP
 - ROMP 102 f., 207, 210, 250, 253, 259
 - rotamers
 - photolysis of 165
 - reactivity of 165
 - syn-anti interconversion 165 f.
 - rotation of the polymer chain 54
 - rotation of the vinyl chain 39
 - Ru(COD)Cl₃ 207
 - Ru(H)(H₂)Cl(PR₃)₂ 208
 - Ru(H₂O)₆(*p*-toluenesulfonate)₂ 207
 - rubber modifier 87
 - RuCl₂(NHC)(PR₃)CHR₁
 - activity 211
 - synthesis 211
 - RuCl₂(PPh₃)₃ 208
 - RuCl₂(PPh₃)₄ 208
 - RuCl₂(PR₃)₂CHR₁
 - activity 208
 - geometry 209
 - synthesis 208

- tolerance of functionality
- use in ADMET 210
- RuCl_3 207
- ruthenium allenylidenes 180
- ruthenium-based alkylidines 161
- ruthenium metathesis catalysts 103, 207
 - carbene fragment in 219
 - decomposition 223
 - N-heterocyclic carbene ligand in 217
 - phosphine ligand in 214, 217, 223
 - exchange 172
 - reactivity order 172
 - stereochemical aspects 221
 - substitution of the chlorides 171
- ruthenium-methylidenes 173

s

- salicylaldimine ligands 75, 226
- SANPAC *see* poly(styrene-acrylonitrile)-based polyacetylenes
- scavengers 82
- Schrock carbenes 204, 209
- Schrock catalysts *see* molybdenum metathesis catalysts
- Schulz-Flory distributions 11
- secondary metathesis *see trans*-metathesis
- self-metathesis 195
- self-branching effect 14
- Shell 145, 239
- Shell Higher Olefin Process 28
- shielding of the metal center and chain transfer 45
- SHOP olefin oligomerization catalysts 28, 79
- SHOP *see* Shell Higher Olefin Process
- short-chain branches 40
- silsesquioxanes 163
- single-component catalysts 30
- specialty polymers 183
- spiroketal structure 298
- square planar coordination 49, 76, 80
- square pyramidal coordination 67
- stereoblock copolymer 291
- stereochemistry 5
 - of ligands 296
- stereoregularity 258, 294
 - of copolymers 283
- stereoselectivity
 - monomer insertion 31
 - polymerization reactions 31
 - of ROMP 173
- steric hindrance 43
- steric repulsion 293

- sterically demanding complexes 47 ff.
- Stetter reaction 62
- strained olefins 298
- styrene 237
 - oligomerization with “naked” Ni and Pd catalysts 107
 - substituted derivatives 15
- styrene-terminated oligo-/polyethylenes 15
- styryl end group 15
- surfactants 231 f., 248, 264 f.
 - nonionic 264
- surfmers 254
- suspension 264
- Suzuki
 - coupling 266
 - cross-coupling 32, 40
 - reactions 32
- symmetric catalysts 43
- symmetric diimine ligands 41
- syn-anti interconversion 164
- syndiotactic copolymers 291
- synthetic rubber 250

t

- tactic polymers 161
- tailored Ni and Pd catalysts 27, 50
- telechelic polymers 180
- Telene® 103
- TEM *see* transmission electron microscopy
- temperature
 - softening 16
- TEOS *see* tetraethoxysilane
- termination
 - radical 260
 - reactions 265
 - reagent 258
- terpolymers
 - ethene-1-olefin-CO 241
- tetraethoxysilane 128
- tetramethylammonium chloride 70
- T_g *see* glass transition temperature
- thallium hexafluorophosphate 109 f.
- therapeutic agents 250
- thermoplasts 16
- thermoplastics 103
 - elastomers 294
- Ticona 101, 144
- titanium-alkylidenes 156
- $(\eta^6\text{-toluene})\text{Ni}(\text{C}_6\text{F}_5)_2$
 - norbornene oligomerization with 132
 - norbornene polymerization with 131 f., 135
 - tolerance to functionality 138

TOPASTM cyclic olefin copolymers 101, 144
 titanium-alkylidenes 156
 transformations of polyketones 300
 transmission electron microscopy 248
 triclinic crystals 49
 tricyclohexylphosphine 137f.
 5-triethoxysilylnorbornene 128, 131, 137,
 141, 147
 trigonal bipyramidal geometry 74
 trimethylaluminium-promoted condensa-
 tion 64
 1,7,7-trimethylnorbornene 165
 triphenylmethylium tetra-
 kis(pentafluorophenyl)borate 92
 tris(hydroxymethyl)phosphine 173
 tris(pentafluorophenyl)borane 127, 137f.,
 147
 tungstacyclobutane species 157
 tungsten(VI) alkylidenes 157
 tungsten metathesis catalysts 103,
 203f.
 – phenoxide catalysts 203
 – reaction with functional groups 205
 tungsten oxoalkylidene complex 161

u

ultrahigh molecular weight polyethylene
 (UHMWPE) 13, 39
 ω -undecenyl alcohol 296
 URPAC polyacetylene 18

v

variation of catalysts steric environment and
 branching in polyethylene 55
 Vestenamer *see* polycyclooctene
 vinyl bromide 313ff.
 vinyl epoxides 296
 vinyl halides
 – β -halide abstraction reaction of 315
 – polymerization of 312
 viscosity 233

x

xantphos 176

y

ylide complexes 5, 8
 – of nickel 5ff.
 – – homogeneous catalyst 5
 – – temperature dependence 19
 – – synthesis 6ff.
 – – X-ray photoelectron spectroscopy 8
 ylide ligands 1ff., 4, 13
 – coordination modes 3
 – – Me₃PCH₂ 7
 ylide-type bond 11

z

(Z)-2-butene 297
 Ziegler-Natta polymerization catalysts 18,
 105, 193